Particulate filled polymers; interaction, structure and micromechanical deformations

Ph.D. Thesis

by

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Chapter 1

Introduction

Heterogeneous polymers are used in increasing quantities in all fields of the economy [1-3]. They are present in tools, utensils and devices used everyday at home, in offices or in plants. Parts of our car or washing machine are made of particulate filled or fiber reinforced composites, dental filling is a polymer nanocomposite, packaging films are prepared from polymer blends or multilayered structures, garden furniture usually consists of CaCO$_3$ filled polypropylene (PP), while racing cars, components of airplanes, rockets and helicopters contain numerous parts prepared from advanced composites. And the list is endless. Most of these materials are heterogeneous systems, which practically always consist of several phases. As a consequence, their structure is complicated, interfaces form between the phases and composition alone does not determine properties. Besides structure, the interaction of the phases across the interface is one the factors determining the properties of these materials, thus the study and modification of interfacial interactions are of utmost importance for their further development. With the advance of science and technology and the introduction of new materials the importance of interfacial interactions does not diminish, on the contrary it considerably increases, especially if we think about the rapid development of nanocomposites, in which interfaces of enormous size develop.

Heterogeneous polymer systems can be divided into several categories. For the sake of simplicity and easier understanding, we divide them into three groups, to polymer blends, fiber reinforced composites and particulate filled polymers. The categorization is naturally arbitrary and oversimplified. For example short fiber reinforced composites behave in every respect very similarly to particulate filled polymers containing anisometric particles, while layered silicate nanocomposites are modeled by theories developed for blends, like the Flory-Huggins lattice model. Nevertheless, the classification presented above is acceptable for the purpose of this thesis, in which we focus our attention exclusively on particulate filled polymers. Heterogeneous, multicomponent systems gain application in many fields, because completely new materials having exceptional properties can be developed relatively simply and rapidly by the proper combination of materials. Fiber reinforced composites compete with steel in strength and stiffness, but they are much lighter, an advantage utilized mainly in the aerospace industry. Blends usually have improved impact resistance compared either to the unmodified polymer or to traditional structural materials [4]. In order to understand that statement we simply have to remind the reader to the box or our monitors or television sets, cellular phones or to many other products. Excellent properties combined with easy processing, light weight and low price make these materials exceptionally competitive. Particulate filled polymer form the oldest and most mature class of these heterogeneous materials. Originally, fillers were added to the polymer to decrease price [5]. Recently, the significant increase of compounding cost put more emphasize on the utilization of technical advantages, on the increased stiffness and dimensional stability of these materials. Hybrids containing two or more different components extend the possibilities of heterogeneous polymer systems even further; they usually offer a very good combination of
properties [6-10]. Anisotropic filler particles reinforce the polymer, but properties, including shrinkage depend on direction [9,11,12]. Warpage can be decreased by the introduction of spherical fillers. Similarly, blending with elastomers results in increased impact resistance, but decreased stiffness; modulus and dimensional stability can be improved by the introduction of particulate fillers like CaCO$_3$ or talc. The advantages of these multicomponent, multiphase materials are amply demonstrated by their growth rate which exceeds that of the economy, generally and also the application of unmodified polymers, particularly. Wood flour filled thermoplastics demonstrate this trend very well, their growth rate in the US was 12% in 2001 [13] and a similar increase is expected in Europe in the future.

As mentioned above, particulate filled polymers represent the largest, oldest, and maybe the most important class of heterogeneous polymer systems. Today primarily their engineering advantages make them attractive, but mineral fillers are cheaper than the polymers, thus occasionally economical advantage can be also gained like in the case of PVC compounds [14]. In spite of the considerable effort of researchers and the industry to find new fillers and reinforcements, the variety of fillers applied in industrial practice is surprisingly limited. CaCO$_3$ is used in the largest quantities, mainly in PVC, but also in other thermoplastics like PE and PP, and in thermoset matrices like in SMC and BMC compounds. The consumption of other fillers, like talc, glass fiber, wollastonite, kaolin, mica, and barite is much smaller (see Table 1.1). The latter, for example, is used in special application areas, where its large density can be utilized advantageously. Extruded plates are prepared from this filler for vibration and sound damping in buses used in public transportation. The number of matrix polymers is similarly limited, mainly because of the effect of fillers on their properties. Mostly commodity polymers are modified with fillers, but occasionally various thermoset materials also contain fillers in their formulation, as mentioned above. The largest quantity of filler, mostly CaCO$_3$ is used in PVC, because its processing technology contains a homogenization step, in which the filler can be introduced without additional effort or expense. Naturally, this possibility results in decreased price and serious advantage for particulate filled PVC products. Although the same possibility of easy introduction does not exist for PE and PP, considerable amount of filler is used also in these polymers. Garden furniture and bumper materials are good examples, but household appliances and car parts are also prepared from particulate filled PP. The filler used in the largest quantity in PP is talc, because of its nucleating effect and reinforcing ability. A very interesting and emerging application of particulate filled PE is the production of breathable films used as the back sheet of diapers as well as in other sanitary applications. The appearance and growth of this product in the market proved that high-tech products can be prepared from very simple materials, but also called attention to the need of further research in the field of particulate filled polymers [15]. Because of the long history and extensive use of these materials, all factors determining their properties are supposed to be known and they are assumed to have simple structure. However, in practice numerous questions have not been answered yet, especially those related to structure formation and to interactions. The efficient production of breathable films, for example, requires a deep knowledge of the effect of interfacial interactions on structure, on micromechanical deformation processes and generally on the macroscopic properties of the composite.
Table 1.1 \textit{Consumption and application of the most important fillers for thermoplastics processing in Europe in 1999} [16]

<table>
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<th>Filler</th>
<th>$\Sigma$ Consumption (Kilotons)</th>
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<tr>
<td></td>
<td></td>
<td>PVC</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>1025</td>
<td>850</td>
</tr>
<tr>
<td>Talc</td>
<td>130</td>
<td>-</td>
</tr>
<tr>
<td>Kaolin</td>
<td>20</td>
<td>13</td>
</tr>
<tr>
<td>Mica</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>7</td>
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The same factors determine the properties of all heterogeneous polymer systems irrespectively of their components, i.e. component properties, composition, structure and interaction [17]. The effect of these factors is easy to understand, nevertheless they are often not considered during the development of new materials. The influence of component properties is obvious, e.g. fibers and fillers increase the stiffness of PP, while the introduction of an elastomer results in decreased modulus and increased impact resistance. It is also evident that the effect of the second component depends strongly on its amount in the system. Usually we want to introduce as much from it as possible into the matrix polymer in order to reach the goal of modification. However, filler loading often has limits, because of the disadvantageous effect of the second component on other than the targeted property. Moreover, the effect of other factors, like structure or interaction also changes with increasing extent of modification, which further complicates the optimization of properties as well as product design. A large variety of structures can develop in heterogeneous polymers. As mentioned above, the morphology of particulate filled polymers is thought to be simple and it is a factor often neglected completely. However various structure related phenomena may occur in these composites, i.e. segregation of the filler during processing, the aggregation of small filler particles or the orientation of filler with anisotropic particle geometry. Moreover, all these structural phenomena, both their occurrence and extent, depend very strongly on filler content. Aggregation is one of the most serious problems in the production of particulate filled polymers, it complicates processing, deteriorates aesthetics as well as the properties of the product. Even more limited is our knowledge about the effect of interfacial interactions on the properties of heterogeneous polymer systems. Interaction leads to the spontaneous formation of an interphase, which has properties different from those of the components. An obvious consequence of interphase formation is the increase in the stiffness and rigidity of the composite, and the dependence of maximum packing fraction, i.e. the amount of filler which can be introduced into the polymer, on particle size. Interactions and the formation of the interphase influence, occasionally determine, micromechanical deformation processes, and thus the final properties of the product. This thesis focuses on two of the above mentioned factors, on interfacial inter-
actions and structure, as well as on the consequences of their modification. Accordingly, these questions are introduced more in detail in the following paragraphs.

As a first approximation, one could assume that the interface is a well defined area with only two dimensions. However, as mentioned above, in particulate filled polymers an interphase forms by the adsorption of the polymer on the surface of the inclusion [18-22]. Although the formation of an interphase is an accepted fact today, considerable debate is going on about its thickness and properties. The interphase can be characterized by a large number of methods and numerous attempts were and are done to do so. Spectroscopic methods are used for the characterization of the chemical composition of surfaces and interphases, as well as to follow the effect of surface modification. Such methods like X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES), diffuse reflectance infrared spectroscopy (DRIFT) and other methods have different resolution and penetration depth [23-27]. However, it is very difficult to obtain information about interphases which form by adsorption or interdiffusion. If the interaction forces are weak – sometimes only dispersion forces act between the components – spectroscopic methods do not help in their detection and even less in the determination of their strength. The effect of the interphase on the properties of a multicomponent material depends on its amount and characteristics. These latter depend very much on the mechanism of interphase formation and on the properties of the components. If the interphase forms by physicochemical interactions, its thickness is determined by the strength of the interaction, while its properties by the characteristics of the components. Besides the strength of interaction, the amount of material bonded in the interphase also influences the properties of the material. Opinions are divided about the properties of the interphase even in such simple materials as silica filled PE. According to some sources a soft interphase forms in such composites, while others claim the formation of a hard interlayer [22,28]. The importance of interactions is shown by the numerous attempts to modify them. According to their mechanism surface modifications can be classified into four groups: non-reactive treatment or coating [29-31], reactive treatment or coupling [10,19,32-35], the use of a functionalized polymer, or the coverage of the filler or fiber with an elastomer layer [21,36]. Much confusion is related already to the goals and aspects of modification, but also the effect is unclear. The surface of fillers can be modified in order to decrease their surface free energy, which hinders aggregation, but decreases also matrix/filler interaction. Occasionally interaction must be improved to avoid debonding and failure, coupling or a functionalized polymer should be applied in such cases. However, reactive modification is seldom used in particulate filled polymers because of its price and effect (increased stiffness and brittleness) and because the main goal of treatment is usually the prevention of aggregation. The easiest and cheapest way to reach this goal is the application of non-reactive treatment [37,38]. Although surface modification appears to be a simple process, much contradiction is associated with the selection of the surfactant or the coupling agent, its amount as well as with the effect of treatment on the surface characteristics of the filler and on the properties of the composite. Some of these issues are addressed in this thesis.

We listed above the most important structure related phenomena occurring in particulate filled polymers. Under practical conditions segregation of the dispersed
phase does not occur or its extent is negligible, but the other two processes, aggregation and the orientation of anisotropic fillers may influence the properties of composites significantly [39]. Orientation of short fibers or fillers with plate-like geometry parallel to the direction of external load is beneficiary; the part is reinforced by the filler, its stiffness and strength increase. As a consequence, orientation is a frequently studied phenomenon and considerable information has been published in the literature about its effect on composite properties [9,39-43]. On the other hand, even the detection of aggregation is difficult, but the characterization of its extent, as well as the determination of all the factors influencing its occurrence are problems, which have not been resolved yet. However, aggregation has enormous practical importance, because aggregates may block filters and decrease productivity, result in bad surface characteristics and poor mechanical properties. The fracture resistance and especially the impact properties of composites may deteriorate significantly when considerable aggregation occurs during the preparation of particulate filled composites [38,44-46]. Although experience indicates that the aggregation tendency of fillers increases with decreasing particle size, increasing surface energy and lower shear forces, other factors may exist, which influence its extent [47]. Moreover, quantitative correlations between the extent of aggregation and various composite properties do not exist at all. The determination of such correlations is further complicated by the fact that composite preparation changes all properties of the polymer and more than one phenomena occur, the combination of which determine final composite characteristics. The separation of such phenomena is difficult, if not impossible, although the selection and control of the dominating one would facilitate production and improve the properties of the product. Such questions are discussed in the second part of the thesis.

As described in the previous two paragraphs interfacial interactions and structure strongly influence, basically determine the properties of particulate filled composites. These two factors control also the micromechanical deformation processes taking place during the deformation of the material. Under the effect of external load complicated stress distribution develops around the inclusions, which initiates local deformation processes [48]. Four micromechanical deformation processes may take place in heterogeneous polymers, in polymer blends and particulate filled polymers, i.e. shear yielding, crazing, debonding and cavitation. Additional, fiber related processes, like fiber pull out, buckling, fracture, etc., may occur in short and long fiber reinforced composites. Bundles of molecules or crystalline units slip during shear yielding leading to considerable plastic deformation and energy consumption [49]. Crazing is the characteristic deformation process of impact modified PS, which consists of the formation and elongation of fibers connecting the lips of the craze. Crazing also consumes much energy, but unlike shear yielding it is accompanied by a volume increase. Cavitation may occur during the deformation of elastomer modified, impact resistant polymers, like PA, epoxy or PP. The large hydrostatic pressure developing in the material during deformation tears apart the elastomer droplets dispersed in the polymer matrix and leads to the development of voids. The dominating deformation process of particulate filled polymers is debonding, the separation of the matrix/filler interface [50]. Easy debonding leads to inferior properties and the premature failure of the composite. Breathable film technology uses this process for the production of the films. Voids of controlled size, which make possible the permeation of vapor, but hinder the transport of liquids are
formed during the stretching of PE films containing a large amount of particulate filler. The detailed knowledge of the debonding process facilitates the selection of the components, the determination of the best composition, as well as processing and stretching conditions. However, usually not only one, but several micromechanical deformation processes take place simultaneously in particulate filled composites. Accordingly, considerable shear yielding may also occur besides debonding. The relative magnitude of the two processes is not known, and neither is their individual effect on film properties, like impact resistance or vapor transmission. The latter property is of crucial importance in the production of breathable films, which is determined by the number and size of voids formed during stretching. One of the goals of the thesis was to obtain quantitative information about the debonding process and the factors influencing it, mainly about the effect of structure and interfacial interactions.

It is obvious from this introductory section that this thesis focuses attention on two main questions, on interfacial interactions and structure developing in particulate filled polymers. In order to obtain a more extensive knowledge about interactions, methods suitable for their characterization had to be studied and analyzed in detail. Besides the processing of information available in the open literature, we had to develop our own procedure for the measurement and evaluation of interactions in the composites studied by us. Proper surface characterization and surface modification of fillers helped to find correlation between interaction and composite properties, but also to study structure-property correlations and micromechanical deformation processes in selected particulate filled polymers. These questions were studied in several well defined subprojects during my PhD studies, which are introduced more in detail in the following paragraphs. However, the goal and basic concept of the work was always the study of interactions, structure and micromechanical deformation processes and the determination of quantitative correlations among them if possible.

Accordingly, Chapter 2 focuses attention on the reliable determination of a parameter, which can be used for the quantitative characterization of the strength of interfacial interactions in particulate filled polymers. Earlier studies proved that the best candidate for this purpose is the reversible work of adhesion, which can be calculated from the surface characteristics of the filler, from its surface tension and electron acceptor and donor characteristics. Recently the thermodynamic characteristics of solid surfaces are determined mainly by inverse gas chromatography, but several theoretical and practical problems hinder the application of the technique. Mineral fillers, including CaCO$_3$ have high energy surfaces, which adsorb water. Surface characteristics of fillers containing a significant amount of adsorbed water differ considerably from that of the dry surface, a fact which led to the publication of a wide range of contradictory data. Not only measurement, but evaluation and the calculation of the work of adhesion are also difficult. Acid-base interactions are often neglected, or the method of calculation and the parameters used in them are not defined sufficiently. In an attempt to obtain a better picture about the surface characterization of fillers and the estimation of interfacial interactions, we investigated systematically the effect of sample preparation and measurement conditions on the surface characteristics of fillers. We also compared various approaches and parameters (donor-acceptor numbers of solvents) used in current practice for the calculation of the acid-base characteristics of surfaces and selected
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those, which lead to the most accurate and reliable values. We used CaCO$_3$ as model filler in this study.

The majority of commercial CaCO$_3$ fillers are coated with an organic substance, mainly stearic acid, in order to avoid aggregation, which deteriorates composite properties. Surface treatment decreases the surface tension of the filler, the extent of which, as well as the efficiency of the coating is determined by several factors including the character of the interaction between the surfactant and the filler surface, surface coverage, the structure of the interlayer formed and the interaction of the adsorbed surfactant molecule with the polymer matrix. The structure of the surfactant layer depends on the orientation of the organic molecules adsorbed on the filler surface, which, on the other hand, is influenced by their chemical structure and surface coverage. Since only a limited number of studies have been carried out to determine the adsorption of carboxylic acids on fillers generally, and even less on CaCO$_3$ in spite of the practical importance of this filler, the study reported in Chapter 3 focuses on these issues. Earlier results indicate clearly that the amount of adsorbed surfactant depends on the specific surface area of the filler. Saturated carboxylic acids are attached to the surface through their acidic functionality, orientated vertically to the surface, and surface coating leads to a decrease in the surface polarity of the filler. We used inverse gas chromatography to investigate the adsorption of mono- and dicarboxylic acids on the surface of CaCO$_3$ as well as the changes in surface free energy as an effect of coating. The structure of the surfactant was varied considerably, surfactants with various chain length, chemical structure (branched, unsaturated) and with different number of acidic moieties were used for the coating of the filler. The amount of acid necessary for monolayer coverage was determined from the measured data and an attempt was made to draw conclusion from the IGC experiments about the orientation of the surfactant molecules and about the structure of the adsorbed layer.

We explained earlier that interfacial interactions lead to the spontaneous formation of an interphase in particulate filled polymers. The amount of the polymer bonded in the interphase depends on the size of the contact surface between the polymer and the filler, i.e. on the specific surface area of the filler, and on the strength of the interaction. The thickness and properties of the interlayer cannot be measured directly and the effect of the strength of interaction on interphase thickness is not known either. In Chapter 4, we make an attempt to find a correlation between the two quantities. Interfacial adhesion of the polymer matrix and the filler results mostly from secondary, van der Waals forces, including dispersion, dipole-dipole, induced dipole etc. forces. Dispersion forces are taken into account in all theories directed towards the determination of the strength of interaction, but different approaches are used for the estimation of the effect of other forces. Interactions in polar systems are described either by dipole-dipole or by acid-base interactions. In this part of the work we estimated the effect of specific interactions on interphase formation in particulate filled polymers. Uncoated and surface treated CaCO$_3$ was introduced both into acidic and basic polymers and the reversible work of adhesion was calculated by both approaches mentioned above. The thickness of the interphase was deduced from mechanical properties and compared to the work of adhesion. The results obtained by the different approaches are discussed in the chapter.
In the general part of the introduction we described the structure related phenomena, which may possibly occur in particulate filled polymers. The structure of semi-crystalline polymers, including polypropylene (PP), is relatively complicated in itself. Crystal modification, crystallinity and the size as well as size distribution of the crystalline units (lamellae, spherulites) may vary in a wide range with changing sample preparation and processing conditions. The introduction of a second component into PP usually further modifies morphology. Fillers may act as nucleating agents changing the thermodynamic and kinetic conditions of crystallization. Often specific morphology develops in the composites; anisotropic particles are usually orientated in different extents, while spherical fillers frequently form aggregates. Because of the considerable number of factors influencing the structure and properties of particulate filled polypropylene, the views concerning their effect are often contradictory. Talc and CaCO$_3$ are used in large quantities for the modification of PP. The two fillers have different particle geometry and dissimilar effect on the crystalline structure of PP. CaCO$_3$ consists of more or less spherical particles and influences crystallization only slightly, while talc has plate-like geometry and a strong nucleation effect. The properties of the composites prepared with the two fillers are also different; however, it is still debated whether the changing crystalline structure of the matrix, nucleation, or anisotropy and orientation of the filler cause the observed differences. In the first part of Chapter 5 we give an overview about the factors influencing the properties of particulate filled polymers with special attention to the correlation of structure and properties. Subsequently we present a case study, which shows the effect of various factors acting simultaneously in particulate filled PP and propose a method for the separation of these effects.

Significant aggregation did not occur in the composites discussed in Chapter 5. However, particle/particle interactions may lead to the formation of aggregates. The occurrence and extent of aggregation depend on the relative magnitude of adhesion and separating forces. The former is determined by the surface tension of the filler and its particle size, while the latter depends on the level of shear forces. Commercial grades of CaCO$_3$ usually have a wide particle size distribution. Consequently, a fraction of the small particles always aggregates, while large particles are distributed separately. The unambiguous determination of aggregation is difficult. Previous results have shown that aggregation always occurs below a certain particle size or above a certain specific surface area. In PP composites, the critical value proved to be 5-7 m$^2$/g. Aggregation modifies stiffness only slightly but strength and impact resistance depend very much on structure, both decrease with increasing extent of aggregation. The mode of failure initiation also depends on particle size, debonding is the dominating deformation mechanism in composites containing large particles, while cracks are initiated inside large aggregates forming at small particles sizes. Contradictory results were obtained concerning the effect of processing, injection molded specimens were not always more homogeneous than compression molded ones. In Chapter 6 we analyze the results obtained on PP/CaCO$_3$ composites in order to characterize the structure of the composites quantitatively by optical microscopy, compare the results to mechanical properties and especially to fracture characteristics and identify the most important factors influencing aggregation. We also made an attempt to resolve the contradiction concerning the effect of processing technology, which was observed in our earlier study.
As described earlier, in particulate filled polymers the dominating deformation mechanism is the separation of the matrix/filler interface, i.e. debonding, which leads to a volume increase during deformation. Several attempts were made earlier to describe this mechanism quantitatively. Models were developed, which predict the conditions for the initiation of debonding, attempts were made to predict the number of debonded particles and the growth of voids was also described in a paper. Although the debonding process was studied earlier by several authors its concise analysis has never been carried out in the past. In Chapter 7 we analyze the separation of matrix/filler interface in polyethylene composites containing various amounts of CaCO$_3$ filler. Debonding was determined by the measurement of volume increase during deformation and the results are critically analyzed in view of existing theories. The most important factors governing void formation, as well as the number and size of the created particles are pointed out as a result of the analysis.

In the final chapter of the thesis, in Chapter 8, we briefly summarize the main results obtained during the thesis, but refrain from their detailed discussion, because the most important conclusions were drawn and reported at the end of each chapter. This chapter is basically restricted to the listing of the major thesis points of the work. The large number of experimental results obtained in the research supplied useful information and led to several conclusions, which can be applied during the production and use of particulate filled composites. Nevertheless, several questions remained open in the various parts of the study, their explanation needs further experiments. Research continues in this field at the department and we hope to proceed successfully further along the way pointed out by this thesis.

References

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Chapter 2

Determination of the surface characteristics of particulate fillers by linear IGC

2.1. Introduction

As mentioned earlier the properties of particulate filled polymers are determined by the characteristics of its components, composition, structure and interfacial interaction. The effect of this latter factor depends on the size of the interface and the strength of the interaction, which is proportional to the reversible work of adhesion calculated from the surface characteristics of the filler [1-4]. Work of adhesion can be derived from the surface tension as well as the electron acceptor and donor characteristics of the surface. In recent years the thermodynamic characteristics of solid surfaces are determined mainly by inverse gas chromatography [4-24]. However, obtaining reliable parameters by this technique is rendered difficult by several theoretical and practical problems. The measurement of the surface characteristics of minerals with high-energy surfaces is especially problematic because of the adsorption of water. This also applies to particulate fillers including CaCO₃, which is used in large quantities in all kinds of applications. The difficulties mentioned above might explain the fact that surface characteristics published in the literature differ significantly from each other and cover a very wide range even for very similar fillers. The comparison of acid-base characteristics published by various groups sources is made even more difficult by the fact that various approaches exist in the literature for the calculation of these thermodynamic characteristics from measured data. This part of our study was directed to the determination the effect of sample preparation and measurement conditions on the surface characteristics of fillers by inverse gas chromatography (IGC) in systematic series of experiments with the intention of defining optimum conditions for their characterization. We also compared various approaches and parameters (donor-acceptor numbers of solvents) used in current practice for the calculation of the acid-base characteristics of surfaces and select those, which lead to the most accurate and reliable prediction. We used CaCO₃ as model filler in this study, since in industry it is used in the largest quantity among all fillers. We believe that the results obtained apply also to other fillers with high surface energy.

2.2. Background

In the first stage of the study we briefly summarize the theoretical background of the determination of surface characteristics by IGC and the approaches used in current practice. We also point out contradictions, which limit the application of these methods.
2.2.1. Surface characteristics: reversible work of adhesion

Interfacial adhesion is created by the interaction of the adsorbed material and the substrate. If interaction is created only by secondary forces, its strength can be characterized by a thermodynamic function, the reversible work of adhesion \( W_A \). This quantity can be divided into two parts: a dispersion term \( W_A^d \) and the one characterizing the specific interactions \( W_A^{sp} \) of the components (electron donor-acceptor or dipol-dipol interactions) [3]

\[
W_A = W_A^d + W_A^{sp}
\]  

Using Fowke’s [1,4] approach the reversible work of adhesion can be defined as

\[
W_A = 2\left(\gamma_1^d \gamma_2^d\right)^{1/2} + n^{ab} f \Delta H_A^{ab}
\]  

where \( \gamma_1^d \) and \( \gamma_2^d \) are the dispersion component of the surface tension for components 1 and 2, respectively, \( f \) is a correction factor close to unity, \( n^{ab} \) the number of interacting acid-base sites located on the surface and \( \Delta H_A^{ab} \) is the enthalpy related to acid-base interaction. The two terms of Eq. 2.2 correspond to \( W_A^d \) and \( W_A^{sp} \), respectively. It also follows from Eq. 2.2 that in order to calculate \( W_A \), i.e. to characterize interfacial interaction quantitatively, we must know the dispersion component of the surface tension of both components, as well as the enthalpy of acid-base interaction.

2.2.2. Dispersion component of surface tension

The IGC technique using infinite dilutions is a fast, accurate and relatively simple method for the study of the energetics of solid surfaces. According to the principle of the method, a column is packed with the solid to be characterized and probe molecules with known thermodynamic characteristics are made adsorbed on its surface. Surface characteristics can be derived from retention times or volumes. With this technique the dispersion component of the surface tension of the adsorbent can be determined in two ways. Both approaches are based on the fact that the free enthalpy of adsorption \( \Delta G_A \) is related to the net retention volume \( (V) \) [5], i.e.

\[
\Delta G_A = -RT \ln V + C
\]  

where \( C \) is a constant depending on the reference state selected, \( R \) is the universal gas constant and \( T \) the temperature of the column. The relationship between \( \Delta G_A \) and \( W_A \) is given by Eq. 2.4

\[
\Delta G_A = N a_{LV} W_A^d
\]  

where \( N \) is Avogadro’s number and \( a_{LV} \) is the molecular surface area occupied by the adsorbate. Normal alkanes interact with other substances only by dispersion forces. If we use them as probe molecules \( W_A^{sp} \) equals zero and the dispersion component of the
surface tension of the stationary phase can be deduced from the cross-sectional area of n-alkanes and from their surface tension by using Eqs. 2.1-2.4. Thus the basic equation of the first approach to determine $\gamma_s^d$ takes the following form

$$-RT \ln V = 2N\left(\gamma_s^d\right)^{1/2}a_{LV}\left(\gamma_{LV}^{d}\right)^{1/2} + C$$  \hspace{1cm} 2.5$$

where $\gamma_s^d$ is the surface tension of the adsorbent to be determined and $\gamma_{LV}^{d}$ is that of the probe.

The second approach to determine $\gamma_s^d$ was proposed by Dorris and Gray [6]. If the value of $RT\ln V$, which is derived from the retention volumes measured with n-alkanes of different chain lengths, is plotted against the number of carbon atoms in their chain, we obtain a straight line, the slope of which is given by Eq. 2.6

$$-RT \ln \frac{V_n}{V_{n+1}} = 2N\left(\gamma_s^d\right)^{1/2}a_{CH_2}\left(\gamma_{CH_2}^{d}\right)^{1/2}$$  \hspace{1cm} 2.6$$

where $V_n$ and $V_{n+1}$ are the retention volumes of n-alkanes with $n$ and $n+1$ carbon atoms, respectively, $a_{CH_2}$ is the surface area occupied by a $-CH_2-$ group and $\gamma_{CH_2}^{d}$ is the surface tension of polyethylene.

2.2.3. Acid-base interaction ($\Delta G_A^{ab}$, $\Delta H_A^{ab}$)

If the adsorbate also enters into interaction with the adsorbent through other than dispersion forces, $\Delta G_A^{ab}$ becomes different from zero. This quantity can also be determined by IGC. Similarly to the reversible work of adhesion (see Eq. 2.1), the free enthalpy created by the interaction of two substances can be also divided into two components, i.e.

$$\Delta G_A = \Delta G_A^d + \Delta G_A^{ab}$$  \hspace{1cm} 2.7$$

and the component associated with acid base interactions is related to the retention volume of a polar probe in the following way

$$\Delta G_A^{ab} = \left(R T \ln V^{ref} + C\right) - \left(R T \ln V + C\right) = -R T \ln \frac{V}{V^{ref}}$$  \hspace{1cm} 2.8$$

where $V$ is the net retention volume measured with the probe, while $V^{ref}$ is the retention volume, which we would measure if the solvent entered only into dispersion interaction with the adsorbent. $V^{ref}$ can be determined from any physico-chemical characteristic of solvents, which is closely related to their dispersion interaction potential, i.e. to their willingness to enter into dispersion interaction with a solid surface. We can choose a hypothetical n-alkane of which the selected physico-chemical quantity corresponds to that of the polar probe used in the measurement; $V^{ref}$ will be the retention volume of this alkane.
The free enthalpy of the acid-base interaction between the adsorbent and a probe can be determined from several physico-chemical parameters. The principle is the same in all cases: the plot of $-RT\ln V$ against the dispersion potential of n-alkanes yields a straight line and $\Delta G_{ab}^{\text{ab}}$ is given by the distance of the $-RT\ln V$ value obtained for the selected polar probe from this baseline. The physico-chemical quantities most often used in the literature for the determination of $\Delta G_{ab}^{\text{ab}}$ are the $a_{LV}(\gamma_{LV}d^{1/2})$ term appearing in Eq. 2.5 [7-13], and the logarithm of saturated vapor pressure ($\log p_0$) proposed by Papirer [14-19]. Occasionally $\Delta G_{ab}^{\text{ab}}$ is determined also from the boiling point of the solvent ($T_b$) [7,20], its molar deformation polarization ($P_D$) [21], the quantity $(h\nu_L)^{1/2}\alpha_L$, where $h\nu_L$ is the ionization potential and $\alpha_L$ is the polarizability of the solvent [22], the topology index $h^t$ [23] and the Kovats index [24].

$\Delta H_{ab}^{\text{ab}}$ can be calculated from free enthalpy values determined at different temperatures, since the two quantities are related to each other by Eq. 2.9

$$\Delta G_{ab}^{\text{ab}} = \Delta H_{ab}^{\text{ab}} - T \Delta S_{ab}^{\text{ab}}$$  \hspace{1cm} 2.9

where $\Delta S_{ab}^{\text{ab}}$ is the entropy of the acid-base interaction of the components. Plotting $\Delta G_{ab}^{\text{ab}}/T$ against $1/T$ yields a straight line with the slope of $\Delta H_{ab}^{\text{ab}}$.

2.2.4. Donor and acceptor numbers

The enthalpy of acid-base interaction ($\Delta H_{ab}^{\text{ab}}$) necessary for the calculation of the reversible work of adhesion can be derived also from the acid-base parameters of the components according to the theories of Drago [25] or Gutmann [26], respectively. The donor-acceptor approach frequently used for the characterization of acid-base interactions was first suggested by Gutmann [26]. He characterised all compounds by an acceptor ($AN$) and a donor ($DN$) number, which indicate the Lewis acid or base character of a given component. According to his theory, $\Delta H_{ab}^{\text{ab}}$ is defined in the following way

$$\Delta H_{ab}^{\text{ab}} = \frac{(AN)(DN)}{100}$$  \hspace{1cm} 2.10

He used different methods for the determination of $DN$ and $AN$. His donor number corresponds to the absolute value of enthalpy change measured by calorimetry during the interaction of a selected compound, a base and a strong Lewis acid, antimony pentachloride ($\text{SbCl}_5$) in an inert solvent. Accordingly, the resulting $DN$ number is given in kcal/mol units. On the other hand, $AN$ is a dimensionless quantity, since it is proportional to the chemical shift of a strong base, triethyl phosphate oxide ($\text{Et}_3\text{PO}$), measured by $^{31}\text{P}$ NMR spectroscopy, when it is dissolved in the investigated acid. Actual $AN$ values can be derived with the help of an arbitrary scale on which 0 is set by the chemical shift of $\text{Et}_3\text{PO}$ in n-hexane, while 100 is obtained for a dilute solution of $\text{SbCl}_5$ in 1,2-dichloro ethane. The value of 100 in the denominator of Eq. 2.10 accounts for the difference caused by the dissimilar techniques used for the determination of $AN$ and $DN$. 


Because of the complications caused by the different techniques of
determination and the resulting dissimilar dimensions of the $AN$ and $DN$ values
obtained, often modified parameters are proposed and used in practice. Riddle and
Fowkes [27] proved that a distinct shift can be measured in the $^{31}$P NMR spectrum of
Et$_3$PO also in completely apolar liquids, like n-hexane, which interact only by
dispersion forces. As a consequence, the $AN$ parameter determined by the technique of
Gutmann [26] must be corrected; the value obtained after correction, $AN - AN^d$, is also
dimensionless, but now it is related only to the acceptor character of the given
compound. The problem of the different dimensions of $AN$ and $DN$ can be also solved
by taking into account the enthalpy change associated with the interaction of the two
reference compounds (SbCl$_5$ and Et$_3$PO) used in Gutmann’s [26] theory. In this case the
corrected $AN - AN^d$ value is expressed in kcal/mol units and denoted as $AN^\prime$.

Ma et al. [28] proposed the normalization of the donor and acceptor parameters
suggested by Gutmann in order to bring them to the same scale. They used the reference
compounds of Gutmann for normalization. Since the enthalpy change created by the
interaction of Et$_3$PO and SbCl$_5$ is 40 kcal/mol ($DN$) and the $AN$ value of SbCl$_5$ is 100 on
Gutmann’s scale, the factors to modify both scales are 2.5 and 0.4 respectively, i.e. the
modified parameters are given as

$$DN^\prime\prime = \frac{100 \cdot DN \text{ (kcal/mol)}}{40 \text{ (kcal/mol)}} = 2.5 \cdot DN$$  \hspace{1cm} 2.11

$$AN^\prime\prime \text{ (kcal/mol)} = \frac{40 \text{ (kcal/mol)} \cdot AN}{100} = 0.4 \text{ (kcal/mol)} \cdot AN$$  \hspace{1cm} 2.12

The modified $AN$ parameter, i.e. $AN^\prime\prime$ is obtained in kcal/mol units, while $DN^\prime\prime$ is a
dimensionless quantity. Donor and acceptor numbers determined by the different
approaches described above are listed in Table 2.1 for the solvents used as probes in our
study.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$AN$ (kcal/mol)</th>
<th>$AN^\prime$ (kcal/mol)</th>
<th>$AN^\prime\prime$ (kcal/mol)</th>
<th>$DN$ (kcal/mol)</th>
<th>$DN^\prime\prime$</th>
<th>$AN - AN^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-alkanes</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>THF</td>
<td>8.0</td>
<td>0.5</td>
<td>3.20</td>
<td>20.0</td>
<td>50.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>3.9</td>
<td>1.4</td>
<td>1.56</td>
<td>19.2</td>
<td>48.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Chloroform</td>
<td>23.1</td>
<td>5.4</td>
<td>9.24</td>
<td>0</td>
<td>0</td>
<td>18.7</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>9.3</td>
<td>1.5</td>
<td>3.72</td>
<td>17.1</td>
<td>42.8</td>
<td>5.3</td>
</tr>
</tbody>
</table>
Eq. 2.10 indicates that if we know the $AN$ and $DN$ values of two interacting substances, the enthalpy of acid-base interaction can be determined. Similarly, if we measure $\Delta H_{ab}$ when a fluid with known acid-base constants interacts with a substrate having unknown characteristics, we can calculate the acid-base parameters of the latter.

Based on Gutmann’s theory [26] Papirer [14,15,29] proposed Eq. 2.13 to describe the interaction of a solid and a fluid for amphoteric materials, which have both acidic and basic character:

$$\Delta H_{ab} = \frac{AN_sDN + DN_sAN}{100}$$  \hspace{1cm} (2.13)

where $AN_s$ and $DN_s$ are the acceptor and donor number of the solid, while $AN$ and $DN$ are those of the fluid used for the measurement. The goal of IGC measurements is often the determination of the acid-base parameters of the adsorbent through the measurement of $\Delta H_{ab}$. Eq. 2.13 is frequently used for the determination of the acid-base constants of polymers and inorganic materials [17,21], but it is often expressed and applied in a modified form [7-10, 16, 20, 22-24]:

$$\Delta H_{ab} = K_aDN + K_dAN$$  \hspace{1cm} (2.14)

where $K_a$ and $K_d$ are constants characterizing the acidity or basicity of the solid surface, while $AN$ and $DN$ the acceptor and donor numbers of the fluid used as polar probe. Occasionally other approaches are also published in the literature, but they have not gained general acceptance yet [18].

According to Eqs. 2.13 and 2.14 the acid-base constants of a solid surface can be determined by the measurement of $\Delta H_{ab}$ associated with the interaction between the solid and various fluids having known acid-base parameters. If we plot the value of $\Delta H_{ab}/AN$ against $DN/AN$, we obtain a straight line, the slope and intersection of which yield the acceptor and donor numbers of the solide, respectively. However, it is not completely clear which of the above discussed $AN$ and $DN$ values (e.g. $AN-AN_e$, $AN^*$, $AN^{**}$, etc.) should be used in the calculations (see Table 2.1). Gutmann’s parameters were used almost exclusively earlier [8,16,17] and they are applied sometimes even these days [23], but because of their deficiencies discussed above, various modified numbers are utilized more frequently in recent years [7,10,18,20-22]. Although the acid-base characteristics of solids should be derived from $\Delta H_{ab}$, some authors report values determined from $\Delta G_{ab}$ [9,11,21,22]. These constants cannot be compared to those calculated from $\Delta H_{ab}$ and contrary to the $K_a$ and $K_d$ values, they depend on temperature and include an entropy term as well.

These considerations clearly indicate that the acid-base parameters of solid surfaces derived from IGC measurements depend largely on the approach and on the $AN$, $DN$ reference values used. In publications focusing on the determination of acid-base parameters by IGC, the calculation technique applied is not always unambiguous, and sometimes the authors do not define even the units of the reported acid-base
parameters [8,9,12,16,17,22,23]. As a consequence one of the main goals of our study was to check the reliability of the various approaches and acid-base parameters used in current practice.

2.2.5. Surface characteristics of coated and uncoated CaCO$_3$

The surface characteristics of CaCO$_3$ fillers have been studied both by linear and finite dilution IGC since many years [9,12,17,19,30-35], but results published in the literature are often contradictory. One of the reasons for the contradictions is that the measured values are significantly influenced by the amount of water adsorbed on the high-energy surface of the filler. In order to remove water, inert gas is passed through the column at high temperature for various lengths of time. Similarly to calculation methods, publications are often rather vague also about the conditions of the preparation and conditioning of the column. They do not give the temperature and time of conditioning [9,12,17], sometimes only the reported low surface energy indicates that it was not preconditioned at all [12]. The conditions of pretreatment reported in the literature cover a wide range, temperatures of 100-200 °C and times of 2-24 hours are used the most frequently [19,33,34,35]. The dispersion component of surface tension determined at 50-100 °C is around 50-60 mJ/m$^2$ [17,19,34,35]. Authors are often unaware of the fact that at high measurement temperatures water can be desorbed from the surface of the filler also during the run itself. The first comprehensive study on the effect of preconditioning and measurement conditions on the surface characteristics of CaCO$_3$ was published in 2000 by Keller et al. [36]. They found that the $\gamma_s^d$ values of various fillers increase continuously with increasing preconditioning temperature and measurement time as an effect of water desorption. Using high preconditioning temperatures led to a $\gamma_s^d$ value as high as 250 mJ/m$^2$ for certain samples, compared to the initial value of 50 mJ/m$^2$, which was determined after preconditioning the column at 50°C. The effect of preconditioning temperature was much less drastic for other samples. Although considerable work has been done on the characterization of CaCO$_3$ by IGC, the number of papers reporting acid-base numbers is relatively small. In most cases, the authors use various polar solvents and give only the $\Delta H_{\text{ab}}$ and $\Delta G_{\text{ab}}$ values associated with the acid base interaction of the components [9,12,17,31,33]. The few $K_a$ and $K_d$ parameter pairs published are not unambiguous either, the thermal history of the filler is often unknown or the way of their determination and calculation of the parameters remains obscure [9,12].

Several papers focused also on the surface characterization of CaCO$_3$ fillers coated with stearic acid [17,19,31-35]. Basically all authors agree that both the dispersion component of the surface tension and surface polarity decrease as an effect of surface treatment [17,19,31,33-35]. However, the extent of this decrease is contradictory again. In order to obtain accurate and reliable surface characteristics of coated and uncoated CaCO$_3$, we must use a reproducible measurement technique as well as well defined conditions. We must know the effect of column pretreatment and measurement conditions on the characteristics derived, and be aware of the influence of the calculation method used. If we can obtain reliable surface characteristics, we are able to predict the strength of interfacial interactions developing in polymer composites and their effect on composite properties.
2.3. Experimental

A commercial CaCO$_3$ filler (Omyacarb 2 GU, Omya, Switzerland) was used throughout the study. Its average particle size is 3.6 µm, its specific surface area 3.6 m$^2$/g. The filler was coated with various amounts of stearic acid in order to achieve surface coverage from 0 to 300 % [34]. The treatment was carried out in a Haake Rheomix 600 internal mixer fitted with blades, for powder mixing. The mixer was driven by a Haake Rheocord EU 10 V unit. In this procedure 80 g filler was preblended with the necessary amount of surfactant, then introduced into the mixer at various temperatures and homogenized at 100 rpm for 10 minutes. The temperature of coating was 120 °C. The dispersion component of the surface tension of uncoated and coated fillers were determined by infinite dilution IGC using n-alkanes with different chain lengths. The acid-base parameters of the filler were measured with chloroform, diethyl ether, ethyl acetate and tetrahydrofurane. All solvents used were of chromatography grade. The acid-base constants of the solvents used in the calculations are listed in Table 2.1, other necessary information can be found in Ref. 9.

IGC measurements were carried out using a Perkin Elmer Autosystem XL apparatus with columns of 50 cm length and 6 mm internal diameter. Before column preparation the filler was aggregated by suspending it in methanol, then drying at 110 °C in an oven. The ground filler was sieved and the fraction between 800 and 1000 µm was used as packing. The amount of vapor injected into the column changed between 0.5 and 20 µl; methane was used as marker and retention peaks were recorded by a flame ionization detector (FID) detector. High purity nitrogen was used as carrier gas and its flow rate changed between 5 and 20 ml/min depending on measurement temperature and on the type of adsorbent. The temperature of both the injector and the FID was set to 200 °C. Each reported value is the result of three parallel measurements.

In order to determine the effect of measurement conditions, the columns were conditioned at 100, 140 and 180 °C for 16 hours under constant flow of nitrogen. The dispersion component of surface tension was determined using C$_7$-C$_{10}$ alkanes at 70, 100, 120 and 140 °C. A new column was prepared and conditioned separately for each set of experimental conditions. Non-conditioned samples were also characterized by the same technique. The effect of measurement time was checked by injecting n-alkanes onto the column in every 0.5 hours in an interval of 35-50 hours. $\gamma^d$ of the filler was determined by the method of Dorris and Gray [6]. Acid-base parameters of coated and uncoated filler samples were derived from measurements carried out in the temperature range between 100 and 140 °C after a conditioning of 16 hours at 140 °C.

2.4. Results and discussion

The results of the paper are reported in several sections. First we discuss the effect of pretreatment and measurement conditions on surface characteristics measured, then summarize results obtained under standard conditions. The dispersion component of surface tension, as well as acid-base parameters obtained both for coated and
uncoated fillers are reported in separate sections.

2.4.1. Pretreatment and measurement conditions

Fig. 2.1 indicates that an increase in the temperature of conditioning leads to higher surface free energy as a result of the continuous removal of water. The results of Fig. 2.1 were obtained at 100 and 140 °C at 0 min measurement time, i.e. immediately after conditioning. The two full circles plotted in the figure represent the values obtained for the non-conditioned sample. The figure clearly proves the pronounced effect of conditioning temperature and explains the large deviations of measured $\gamma_s^d$ values reported in the literature for similar fillers [9,17,35,36]. The dispersion component of surface tension determined at 100 °C is twice as high after conditioning at 180 °C, than that of the sample measured without pretreatment.

![Figure 2.1](image)

**Figure 2.1** Dependence of the $\gamma_s^d$ of uncoated CaCO$_3$ on the temperature of conditioning. Symbols: (●, ■) unconditioned samples, (○, □) conditioned samples, (●, ○) measurement at 140 °C, (■, □) measurement at 100 °C.

Measurement time as well as the relative value of conditioning and measurement temperatures also influence measured surface energies. The results of two series of measurements are plotted in Fig. 2.2 as a function of time. In series 1 the column was conditioned at 180 °C and the measurement was done at 100 °C, while 100 °C and 140 °C were used for conditioning and measurement, respectively, in the second series. High conditioning temperature leads to the desorption of water also from the
high energy sites of the filler surface. However, at a low measurement temperature these
very active sites adsorb traces of water and other contaminations from the probe and/or
the carrier gas, which leads to a continuous decrease of surface energy at longer times.
In the reverse case, at low conditioning temperature water is not removed completely
from the surface, thus continuous desorption of water occurs at higher measurement
temperature, which leads to the increase of surface energy. After 10-15 hours of
measurement, the column reaches equilibrium, surface energy does not change any
more.

Figure 2.2  Effect of measurement time on the γs of uncoted CaCO3. Conditions: (○) conditioning 180 °C, measurement 100 °C, (□) conditioning 100 °C, measurement 140 °C.

Results presented in Figs. 2.1 and 2.2 clearly prove that surface characteristics
determined by IGC for a filler with high surface energy depend on the combination of
pretreatment and measurement conditions; we cannot define conditions resulting in
values which can be regarded as material constants. These results also question the
reliable determination of acid-base constants for CaCO3 and other fillers with high-
energy surfaces. As described in a previous section, ΔG^ab must be measured at various
temperatures if we want to determine ΔH^ab and the K_a, K_d constants. However, the
amount of water adsorbed on the surface of the filler is different various temperatures
leading to dissimilar surface qualities. Naturally, one may question the necessity of the
conditioning of the column, the proper temperature and duration of which is not known.
Conditioning leads to the desorption of water and we obtain a surface with very
inhomogeneous energy distribution of active sites, we also create sites with very high
energies. Since with infinite IGC we measure the most active sites of the surface, this
Surface characteristics of particulate fillers

might bias our evaluation considerably. On the other hand, if we do not condition the column, we measure the energy of a surface covered with water. Moreover, its coverage may change continuously during measurement because of the loss of water. The only solution is the use of standard conditions. The dispersion component of the surface tension of various filler samples must be compared under the same conditioning and measurement conditions. Additionally, the temperature of measurement and conditioning must be kept close to each other in order to achieve constant surface quality, and independence of surface characteristics of measurement time. The dependence of the dispersion component of surface tension on measurement time is presented in Fig. 2.3 for samples conditioned at 140 °C and measured at three different temperatures. \( \gamma_s^d \) is almost independent of time when the measurement is done at 120 °C, and depends on it only slightly even at 100 °C. As a consequence, we may assume that acid-base parameters can also be determined reliably if we measure retention volumes in the range of 100-140 °C. The surface tension of CaCO\(_3\) samples conditioned at 140 °C is plotted against the temperature of determination in Fig. 2.4.

![Figure 2.3](image)

**Figure 2.3** Dependence of the dispersion component of surface tension of uncoated CaCO\(_3\) on measurement time. Temperature of conditioning: 140 °C, temperature of measurement: (□) 70 °C, (○) 100 °C, (△) 120 °C.

We see that the surface free energy of the filler decreases with increasing temperature. However, we may speculate about the actual shape of the correlation presented in Fig. 2.4, \( \gamma_s^d \) values measured at the two lowest temperatures might be much higher in reality, since the adsorption of water may have started already during the adjustment of the measurement temperature. The loss of water during this period may have led to low surface energies.
2.4.2. Surface tension of coated CaCO$_3$

IGC is the ideal technique for the determination of the amount of surfactant resulting in the monolayer coverage of the filler. With increasing surface coverage surface tension is expected to decrease to a minimum, then to increase slightly again [34,37]. Coated CaCO$_3$ probably does not adsorb much water, but partially covered fillers might do, thus in order to ensure identical surface quality, all samples were conditioned at 140 °C for 16 hours and the measurements were carried out at 100 °C. The results are presented in Fig. 2.5. The dispersion component of surface tension decreases up to a certain amount of surfactant, which we identified as monolayer coverage, than it slightly increases again. A similar tendency was observed in a series of measurements carried out by finite IGC [34] in spite of the fact that finite concentration IGC measures average surface energy, while infinite IGC only the most active sites. Minimum surface energy is measured at 0.75-1.0 wt% coating, which agrees well with results obtained on other CaCO$_3$ fillers with a similar specific surface area [34,37]. We assume that monolayer coverage is achieved already at 0.75 wt% concentration of the surfactant, therefore the acid-base parameters of coated CaCO$_3$ were determined at this surfactant concentration.
2.4.3. Acid-base parameters of uncoated CaCO$_3$

In order to obtain the acid-base parameters of CaCO$_3$, first we measured the free enthalpy ($\Delta G_{A}^{ab}$) of adsorption of various polar probes at different temperatures. In order to obtain $\Delta G_{A}^{ab}$, we must create a baseline with n-alkanes capable of only dispersion interaction. We used two of the approaches presented previously to define the baseline: we plotted the $RT\ln V$ values against $a_{LV}(\gamma_{LV}^{d})^{1/2}$ (Method I) or against $\log p_0$ (Method II), respectively. Plotting $\Delta G_{A}^{ab}$ values determined in this way against temperature resulted in straight lines, the slope of which equals $\Delta H_{A}^{ab}$. The procedure followed and the straight lines obtained are presented in Figs. 2.6 and 2.7 for two solvents, ethyl acetate and chloroform. $\Delta H_{A}^{ab}$ values derived are summarized for all probes in Table 2.2 together with the regression coefficients of the lines, from which they were calculated. Figs. 2.6 and 2.7 as well as Table 2.2 indicate that $\Delta H_{A}^{ab}$ can be determined with acceptable accuracy in spite of the difficulties described in previous sections. The regression coefficient of the straight lines exceeds 0.92 in each case. Method I, i.e. the use of the surface tension of the probe molecule as reference quantity, results in somewhat smaller $\Delta H_{A}^{ab}$ values, but the determination is more accurate in this way than by Method II. The results prove again that the absolute value of the surface characteristics of a filler depend on the approach and on the method of determination.
Figure 2.6 Determination of the enthalpy of acid base interaction according to Method I. Symbols: (□) chloroform, (○) ethyl acetate.

Figure 2.7 Determination of the enthalpy of adsorption of polar probes according to Method II. Symbols: (□) chloroform, (○) ethyl acetate.
Table 2.2  Acid-base component of the enthalpy of adsorption of polar solvents on uncoated CaCO₃

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Method I</th>
<th>Method II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔH (kJ/mol)</td>
<td>R²</td>
</tr>
<tr>
<td>Chloroform</td>
<td>25.8</td>
<td>0.9498</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>13.9</td>
<td>0.9691</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>16.8</td>
<td>0.9929</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>9.7</td>
<td>0.9929</td>
</tr>
</tbody>
</table>

Figure 2.8  Determination of the acid-base constants of uncoated CaCO₃ according to Method A.

The acid-base parameters of the filler were calculated from $\Delta H_A^{ab}$ using the $AN$, $DN$ numbers listed in Table 2.1. According to Eq. 2.14 $\Delta H_A^{ab}/AN$ was plotted against $DN/AN$ in order to obtain the $K_a$, $K_d$ parameters. The procedure is demonstrated in Fig. 2.8. The $\Delta H_A^{ab}$ values were determined by Method I, while the $AN^*$ value of Riddle and Fowkes [27] and the $DN$ number of Gutmann [26] were used for the construction of the figure. The calculation, i.e. the determination of $K_a$ and $K_d$
parameters were carried out for all combinations of $AN$, $DN$ parameters proposed in the literature and listed in Table 2.1. The applicability of the constants was judged by the goodness of the linear fit of Eq. 2.14 to the results. A fit with a determination coefficient larger than 0.9 was rated good, while below this number as poor. The parameter pairs used in the calculation and their ratings are summarized in Table 2.3. Poor fit was obtained with the original $AN$, $DN$ constants of Gutmann [26] and with the combination of these parameters and the ones modified by Ma [28]. On the contrary, good linear correlation was obtained in two cases, with the $AN^*$, $DN$ parameter pair proposed by Riddle and Fowkes [27] and Gutmann [26], respectively, and with the $AN$-$AN^d$ and $DN^{**}$ parameter combination. The first pair of parameters yielded $K_a$ and $K_d$ constants as dimensionless quantities, while the use of the second pair leads to quantities with the same physical meaning, but expressed in kJ/mol units.

<table>
<thead>
<tr>
<th>Method</th>
<th>Acceptor number</th>
<th>Donor number</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$AN^*$</td>
<td>$DN$</td>
<td>Gutmann</td>
</tr>
<tr>
<td>B</td>
<td>$AN$-$AN^d$</td>
<td>$DN^{**}$</td>
<td>Ma</td>
</tr>
<tr>
<td>C</td>
<td>$AN$</td>
<td>$DN$</td>
<td>Gutmann</td>
</tr>
<tr>
<td>D</td>
<td>$AN^{**}$</td>
<td>$DN$</td>
<td>Gutmann</td>
</tr>
<tr>
<td>E</td>
<td>$AN$</td>
<td>$DN^{**}$</td>
<td>Ma</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th>A</th>
<th>B</th>
<th>R²</th>
<th>$K_a$ (kJ/mol)</th>
<th>$K_d$ (kJ/mol)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.09</td>
<td>1.33</td>
<td>0.9687</td>
<td>0.14</td>
<td>1.61</td>
<td>0.9566</td>
</tr>
<tr>
<td>II</td>
<td>0.15</td>
<td>1.24</td>
<td>0.7853</td>
<td>0.26</td>
<td>1.49</td>
<td>0.7804</td>
</tr>
</tbody>
</table>

$K_a$ and $K_d$ values calculated from the last two parameter pairs (Methods A and B) are listed in Table 2.4 together with the regression coefficient of the fit. The results of the table indicate that acid-base parameters can be calculated with practically the same accuracy from both pairs of $AN$, $DN$ constants. On the other hand, using the surface tension of the solvent for the characterization of its dispersion interaction potential (Method I) results in lines of much better fit than the use of saturated vapor pressure (Method II). Although the actual value of the acid-base constants differ
somewhat from each other, the donor number exceeds considerably the acceptor number in both cases; the large donor number reflects properly the strong basic character of uncoated CaCO₃.

Table 2.5  Acid-base constants calculated from the free enthalpy of adsorption at various temperatures

<table>
<thead>
<tr>
<th>Measurement temperature (°C)</th>
<th>$K_a'$</th>
<th>$K_d'$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.08</td>
<td>0.24</td>
<td>0.9530</td>
</tr>
<tr>
<td>120</td>
<td>0.08</td>
<td>0.19</td>
<td>0.9357</td>
</tr>
<tr>
<td>140</td>
<td>0.08</td>
<td>0.13</td>
<td>0.9239</td>
</tr>
</tbody>
</table>

As mentioned earlier, acid-base characteristics occasionally are not calculated only from the specific component of adsorption enthalpy, but directly from free enthalpies. The parameters obtained in this way ($K_a'$, $K_b'$) depend on temperature and include also the entropy term of interaction. On the other hand, one measurement at a single temperature suffices to obtain them. This eliminates the possible influence of changing surface quality and saves considerable time. $K_a'$ and $K_d'$ parameters calculated from $\Delta G_A^{ab}$ values measured at various temperatures are listed in Table 2.5. The parameters were derived in a similar way as those in Table 2.4, i.e. fitting Eq. 2.14 to the calculated $\Delta G_A^{ab}/AN^*, DN/AN^*$ data pairs. Method A was used in these calculations. The goodness of the fit is practically the same as when $\Delta H_A^{ab}$ was used for the calculation of $K$ parameters. The larger donor numbers indicate again the basicity of the CaCO₃ filler, but the ratio of $K_d'/K_a'$ is much smaller than that of the corresponding $K$ values and it decreases with increasing temperature. Accordingly, the relative basicity of the filler estimated by this method is much smaller and depend on measurement conditions.

Table 2.6  Acid-base component of the enthalpy of adsorption of the polar solvents used in the study calculated by Method I for the coated filler

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Enthalpy change (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>6.0</td>
<td>0.9489</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>26.6</td>
<td>0.9820</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>38.5</td>
<td>0.9735</td>
</tr>
<tr>
<td>Tetrahydrofurane</td>
<td>35.4</td>
<td>0.9530</td>
</tr>
</tbody>
</table>
Table 2.7  
Acid-base constants of the coated filler derived from the enthalpy and the free enthalpy (100 °C) of adsorption by using donor and acceptor number pairs A and B respectively

| Method | Thermodynamic quantity | Parameter | Value  
|--------|------------------------|-----------|--------
|        |                        | $K_a$     | 0.42   
| A      | $\Delta H_A^{ab}$      | $K_d$     | 0.18   
|        |                        | $R^2$     | 0.9938 
| B      | $\Delta G_A^{ab}$      | $K_a'$    | 0.18   
|        |                        | $K_d'$    | 0.00   
|        |                        | $R^2$     | 0.9941 
|        | $\Delta H_A^{ab}$      | $K_a$ (kJ/mol) | 0.70   
|        |                        | $K_d$ (kJ/mol) | 0.20   
|        |                        | $R^2$     | 0.9927 
|        | $\Delta G_A^{ab}$      | $K_a'$ (kJ/mol) | 0.20   
|        |                        | $K_d'$ (kJ/mol) | 0.00   
|        |                        | $R^2$     | 0.9920 

2.4.4. Acid-base parameters of coated CaCO$_3$

Fig. 2.5 indicates that monolayer coverage of the filler used in this study is achieved at 0.75 wt% stearic acid coating, thus acid-base parameters of the coated filler were determined at this coverage. Measurements were made in the temperature range of 100 – 115 °C, because the $\Delta G_A^{ab}$ value of chloroform was nearly zero above 115 °C. $\Delta H_A^{ab}$ was calculated from the $\Delta G_A^{ab}$ values determined by Method I; the results are listed in Table 2.6. The linear fit is excellent in each case. Acid-base parameters were calculated both from $\Delta H_A^{ab}$ ($K_a$, $K_d$) and $\Delta G_A^{ab}$ ($K_a'$, $K_d'$) by Methods A and B, respectively (see Table 2.7). The surface characteristics of the filler change significantly as an effect of coating, the basicity of the filler decreased considerably. $K_d$ is about tenth of the value of the uncoated filler, while $K_d'$ indicates a complete lack of basicity. On the other hand, the relatively strong acidity of the coated filler is rather surprising. This unexpected increase in surface acidity may be explained by the orientation of the stearic acid molecules on the surface. The amount of stearic acid used may exceed monolayer coverage, the formation of a second layer starts, in which the acidic moiety looks outward. Inhomogeneous coverage may also occur, very active sites may adsorb two layers, while other parts of the filler remain uncoated. However, basicity should be
significantly stronger in the second case, since the uncoated filler had a very strong basic character. Further experiments must be carried out in order to explain the strong acidity of the coated surface and reveal the orientation of adsorbed stearic acid molecules.

2.5. Conclusions

Linear IGC experiments carried out on a coated and an uncoated CaCO$_3$ filler and the following critical analysis of the results proved that this technique can be successfully used for the surface characterization of fillers and other materials with high energy surfaces. The complete characterization of the filler surface requires the determination of the dispersion component of its surface tension and the knowledge of its acid-base character. Because of the high energy of the surface, it readily adsorbs water thus the parameters measured by IGC depend on column preparation and measurement conditions. Because of the combined effect of conditioning temperature and time, as well as measurement conditions, the determined surface characteristics are not material constants. Different type or grade of fillers, or the effect of coating can be compared only under standard conditions. The use of the same conditioning and measurement temperature eliminates the effect of measurement time. Under appropriate standard conditions the acid-base characteristics of the filler can be determined reliably. However, the accuracy of the determination and the value of the derived parameters depend very much on the selected approach and on the acid-base constants used for the solvent. The enthalpy change of acid-base interaction can be determined the most accurately from measured $\Delta G_{A}^{ab}$ values by using the quantity $a_{L}^{i}(\gamma L V_{d})^{1/2}$ describing the dispersion potential of the probe, while the acid-base constants of the filler must be derived from the corrected acceptor number ($AN-AN^{d}$, $AN^{*}$) of Riddle and Fowkes and from Guttmann’s donor numbers ($DN$, $DN^{**}$). The results proved that the surface of the CaCO$_3$ filler used in these experiments is strongly basic in character. Coating significantly reduces basicity. The relatively strong acidic character of the coated filler indicates surface coverage exceeding monolayer coverage and/or the uneven distribution of the surfactant on the surface.

2.6. References

Chapter 2

32. Ashan, T., *Colloids Surfaces* 64, 167 (1992)
Chapter 3

Adsorption of surfactants on CaCO$_3$ and its effect on surface free energy

3.1. Introduction

Particulate filled composites are widely used in many fields of application. The filler applied in the largest quantity is CaCO$_3$, which is added mainly to PVC, but significant amounts are used also in PP, PE and other polymers. Typical products prepared from CaCO$_3$ filled composites are sewer and drainage pipes, garden furniture, breathable films, etc. [1]. The properties of particulate filled polymers are determined by several factors of which interfacial interactions are extremely important [2,3]. Particle/particle and particle/matrix interactions develop in such composites, the first determines the extent of aggregation, while the second the adhesion of the phases. The majority of commercial CaCO$_3$ fillers are coated with an organic substance, mainly stearic acid, in order to avoid aggregation, which deteriorates composite properties. Surface treatment decreases the surface tension of the filler and thus both kinds of interactions [4,5]. The decrease of surface tension and the efficiency of the coating is determined by several factors including the character of the interaction between the surfactant and the filler surface, surface coverage, the structure of the interlayer formed and the interaction of the adsorbed surfactant molecule with the polymer matrix [5,6]. The structure of the surfactant layer depends on the orientation of the organic molecules on the filler surface, which, on the other hand, is influenced by their chemical structure and also by surface coverage [6].

The structure of this layer and the effect of coating on the surface characteristics of particulate fillers can be studied by numerous techniques [7]. Surface analytic techniques like X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), Fourier transform infrared spectroscopy (FTIR), solid-state nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) give information about the orientation of the surfactant molecules and about surfactant/filler interaction [5-10]. Flow microcalorimetry (FMC) and the determination of adsorption isotherms reveal the amount of surfactant adhering to the surface, the strength of interaction as well as its mechanism [7-9]. Various other methods may also be applied to draw conclusions about the efficiency of surface coating like differential scanning calorimetry (DSC), scanning electron microscopy (SEM) [11], infiltration and adsorption of liquids onto the coated filler [12,13] as well as the measurement of composite properties [4,5,15,16]. Although inverse gas chromatography (IGC) is often used [17-20] for the determination of surface free energy, surface coverage and the acid-base character of the coated filler, the measured quantities are rarely related to the structure of the adsorbed layer.

Only a limited number of studies have been carried out to determine the adsorption of carboxylic acids on fillers generally, and even less on CaCO$_3$ in spite of the practical importance of this filler. Liauw et al. [8,9] investigated the adsorption of various saturated and unsaturated carboxylic acids from heptane onto Mg(OH)$_2$ and
Al(OH)$_3$ and found that the amount and the orientation of the adsorbed acids are affected by the structure of the alkyl tail and the number of double bonds in the surfactant molecule. The double bond participates in the adsorption and a looser surface layer forms than in the case of saturated acids. In a similar study, Ottewil and Tiffany [21] came practically to the same conclusion using the rutile modification of titanium dioxide as filler. According to them, at monolayer coverage, stearic acid is oriented vertically to the surface, while the orientation of unsaturated carboxylic acids is less regular. Ivanishchenko et al. [13] studied the adsorption of fatty acids with different chain lengths on CaCO$_3$. They pointed out, that orientation and surface coverage depend also on the length of the aliphatic chains, more surfactant is needed to achieve monolayer coverage from carboxylic acids with shorter chain lengths. All these studies and our earlier results [5,22] indicate that the amount of adsorbed surfactant depends also on the specific surface area of the filler. Saturated carboxylic acids are attached to the surface through their acidic functionality, they are orientated vertically to the surface, and surface coating leads to a decrease in the surface polarity of the filler.

This part of the study was aimed at the use of inverse gas chromatography to investigate the adsorption of mono- and dicarboxylic acids on the surface of CaCO$_3$ and the determination of changes in surface free energy as an effect of coating. In this effort the structure of the surfactant was varied considerably, surfactants with various chain lengths, chemical structure (branched, unsaturated) and with different number of acidic moieties were used for the coating of the filler. The amount of acid necessary for monolayer coverage was determined from the measured data and an attempt was made to draw conclusion from the IGC experiments about the orientation of the surfactant molecules as well as about the structure of the adsorbed layer.

### 3.2. Experimental

**Table 3.1** Characteristics of the surfactants used in the study for the coating of CaCO$_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Molecular weight (g/mol)</th>
<th>Melting temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{10}$COOH</td>
<td>200.3</td>
<td>44</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{16}$COOH</td>
<td>284.5</td>
<td>70</td>
</tr>
<tr>
<td>Behenic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{20}$COOH</td>
<td>340.6</td>
<td>84</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_2$COOH</td>
<td>282.5</td>
<td>16</td>
</tr>
<tr>
<td>2-ethylhexanoic acid</td>
<td>CH$_3$(CH$_2$)$_3$CH(C$_2$H$_5$)COOH</td>
<td>144.2</td>
<td>-59</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>HOOC–COOH · H$_2$O</td>
<td>126.1</td>
<td>101</td>
</tr>
<tr>
<td>Sebacic acid</td>
<td>HOOC(CH$_2$)$_8$COOH</td>
<td>202.3</td>
<td>133</td>
</tr>
</tbody>
</table>
A ground CaCO$_3$ with an average particle size of 1.8 µm and a specific surface area of 4.0 m$^2$/g was supplied by Omya and used in the experiments. The most important characteristics of the surfactants studied are listed in Table 3.1; the compounds include three saturated monocarboxylic acids with different chain lengths, a branched and an unsaturated mono-, as well as two dicarboxylic acids. CaCO$_3$ was treated with different amount of surfactant (0 – 7.0 wt%). The neat CaCO$_3$ filler was coated with the surfactants in a dry-blending process (see in Chapter 2). Instead of a constant temperature, coating was carried out at temperatures 30 °C higher than the melting point of the surfactant. Treatment with 2-ethylhexanoic acid was done at ambient temperature.

The dispersion component of surface tension of the fillers was determined by linear IGC [23,24]. Specific interaction was calculated from the retention time of chloroform. The details of the measurement can be found in Chapter 2. The amount of the irreversibly bonded surfactant was determined by the dissolution technique developed in our laboratory earlier [5,22]. 20 g coated filler was put into 100 cm$^3$ solvent and stirred for 30 min. As soon as the filler settled, the concentration of the coating agent in the solution was determined by FTIR spectroscopy. The solvent usually was CCl$_4$, but occasionally other solvents (THF, CHCl$_3$) had to be used. The amount of dissolved surfactant was determined from the absorbance of the carbonyl vibration appearing in the range of 1716 - 1710 cm$^{-1}$. A calibration curve was prepared and used for quantitative determination. The coated fillers were also studied by differential scanning calorimetry. The measurements were done in the DSC 30 cell of a Mettler TA 4000 instrument. 10 mg samples were measured in oxygen at 10 °C/min heating rate. The thermograms were evaluated both qualitatively and quantitatively to check the presence of free surfactant; in this way the technique can be used for the determination of monolayer coverage.

3.3. Results and discussion

The results of the experiments are presented in three sections. First monolayer coverages determined by various experimental techniques are compared and the methods are evaluated critically. The adsorption characteristics of mono- and dicarboxylic acids, respectively, as well as the effect of adsorption on the surface characteristics of the filler are discussed in the following two, separate sections.

3.3.1. Determination of monolayer coverage

The dissolution technique has been described elsewhere [5,14,17,22] thus we refrain from its detailed discussion here. The adsorption of organic compounds on the surface of particulate fillers can be studied especially well with the method. Dissolution experiments usually yield an adsorption isotherm with a saturation value. The amount of surfactant needed for monolayer coverage ($c_{100}$) can be determined from the isotherm as the value deviating from the straight line indicating irreversible bonding. Both the quality of the isotherm and the accuracy of the determination of monolayer coverage depend very much on the particle characteristics of the filler, on the chemical structure of the surfactant and on the solvent used. The adsorption of stearic acid could be determined
easily and accurately also in this study; isotherms similar to those reported earlier [5,14,22] were recorded also in this case. Because the adsorption of other carboxylic acids occurred in more than one step, monolayer coverage was determined from the first step. The $c_{100}$ values determined by the dissolution technique are compiled in Table 3.2. These values could not be determined unambiguously by this method for dicarboxylic acids thus they are omitted from the table.

**Table 3.2 Monolayer coverage ($c_{100}$) determined by various methods**

<table>
<thead>
<tr>
<th>Carboxylic acid</th>
<th>Dissolution</th>
<th>DSC</th>
<th>IGC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c_{100}$ (mmol/100 g filler)</td>
<td>acid melting peak</td>
<td>Oxidation shoulder</td>
</tr>
<tr>
<td>Lauric</td>
<td>5.0 – 6.0</td>
<td>6.0</td>
<td>–</td>
</tr>
<tr>
<td>Stearic</td>
<td>3.5 – 4.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Behenic</td>
<td>2.4 – 2.9</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Oleic</td>
<td>2.8 – 3.5</td>
<td>–</td>
<td>3.5</td>
</tr>
<tr>
<td>2-ethylhexanoic</td>
<td>–</td>
<td>–</td>
<td>5.6</td>
</tr>
</tbody>
</table>

During the detailed investigation of coated fillers we observed that thermal calorimetry gives valuable information about the quality of coating and the homogeneity of the samples. One or two shoulders or peaks appear on the thermogram recorded by DSC, when the surfactant is overcoated or its distribution is heterogeneous. Further study indicated that these shoulder or peaks belong to the free acid, which is adsorbed on the surface of the filler, but not attached to it by ionic bond. Moreover, an additional endothermic transition can be also detected for acids having a melting peak above room temperature. Typical thermograms are presented in Fig. 3.1 for the filler coated with various amounts of stearic acid. The endothermic peak characterizing the melting of the acid appears at around 71 °C followed by several exothermic transitions. These latter indicate the oxidation of the surfactant, which was proved by measurements carried out in inert atmosphere. Under such conditions all the exothermic peaks were absent. A closer scrutiny of the thermograms clearly indicates that more than one peaks appear only above a certain surface coverage. From the analysis of the results we concluded that monolayer coverage could be determined from the appearance of the transitions belonging to the free acid.

In the case of stearic acid the determination of monolayer coverage is demonstrated in Fig. 3.2 The heat of fusion of the free acid is plotted against the amount of surfactant used for the treatment; the data were taken from the thermograms presented
in Fig. 3.1. The determination of monolayer coverage is clear and unambiguous. Unfortunately the melting peak cannot be used for characterization in case of compounds having a melting temperature lower than room temperature. In this case, the monolayer coverage can be deduced from the appearance of the shoulder related to the oxidation of the free acid. However, degradation reactions depend very much on the structure of the organic compound, thus the shape and intensity of these shoulders and peaks vary from compound to compound. As a consequence, in the case of lauric acid monolayer coverage could not be determined by this second approach at all. Monolayer coverages obtained from the analysis of the thermograms are also included in Table 3.2.

![DSC thermograms recorded on CaCO₃ fillers coated with various amounts of stearic acid. a) 0.5, b) 0.8, c) 1.0, d) 2.0 e) 5.0 wt% stearic acid.](image)

**Figure 3.1** DSC thermograms recorded on CaCO₃ fillers coated with various amounts of stearic acid. a) 0.5, b) 0.8, c) 1.0, d) 2.0 e) 5.0 wt% stearic acid.

IGC is a well-established method for the surface characterization of fillers and fibers. Earlier experiments have shown that the surface tension of fillers treated with stearic acid decrease significantly with increasing surface coverage [4,5,14]. A minimum appears in surface tension as a function of surfactant concentration, then surface free energy starts to increase again when larger amounts are used for treatment. Measurements carried out by various methods proved that the minimum corresponds to the monolayer coverage of the filler by the given surfactant. In this study, the dispersion component of the surface tension of the filler coated with different mono- and dicarboxylic acids was determined by infinite dilution IGC. The dispersion component of surface tension measured on the filler coated with behenic acid is plotted against the amount of acid used for treatment in Fig. 3.3 As mentioned above, surface tension decreases, reaches a minimum value at about 1.2 wt% surfactants concentration, then increases.
again. If we accept that the minimum corresponds to monolayer coverage, the determination of the amount of surfactant necessary to reach this value is easy and accurate. The values obtained in this way are listed in Table 3.2 for all surfactants.

Figure 3.2 Heat of fusion of free stearic acid plotted as a function of the amount of surfactant used for the treatment.

Polar surfaces enter into acid-base interactions with other materials. Such interactions can be characterized by the free enthalpy change of adsorption ($\Delta G_{sp}^{p}$) of polar probes, which can also be determined by IGC from the retention volume of an appropriate solvent. CaCO$_3$ is basic in character and its basicity can be determined by using an acidic solvent; CHCl$_3$ was used in this study. The $\Delta G_{sp}^{p}$ values obtained on behenic acid coated fillers are plotted in Fig. 3.4 as a function of the amount of surfactant used for treatment. The same tendency is observed as in Fig. 3.3 and the minimum appear practically at the same surfactant content. The free enthalpy change of adsorption was determined for fillers coated with all the surfactants studied and the results are listed in Table 3.2.

The comparison of the data compiled in Table 3.2 allows us to draw several conclusions. We see that the amount of surfactant necessary to reach monolayer coverage is different for most of the surfactants, but the differences are not very large.
Figure 3.3  Changes in the dispersion component of the surface tension of CaCO₃ coated with behenic acid as function of the amount of surfactant used for coating.

Figure 3.4  Acid-base character of the filler coated with behenic acid plotted as a function of the amount of surfactant used for the treatment.
Moreover, similar values were obtained with all techniques used for determination. On the other hand, the values deduced from the dissolution experiments are not very accurate, in fact only a range could be defined instead of a single value. The possible use of DSC for the determination of monolayer coverage is limited, it depends on the chemical and physical properties of the surfactant used for the treatment. The most reliable method for the determination of monolayer coverage is IGC. The technique could be used in each case, independently of the coating agent applied. Even better agreement can be reached between the values derived from the dispersion component of surface tension and the term characterizing specific, acid-base interactions, respectively, if these quantities are determined at a larger number of surface coverages than in the present study. Surface tension could be measured also on fillers coated with dicarboxylic acids, but the determination of monolayer coverage was difficult because of the peculiar adsorption character of these acids.

![Surface tension graph](image)

**Figure 3.5** Effect of the length of the aliphatic chain and the amount of surfactant on the surface tension of CaCO$_3$ coated with various monocarboxylic acids. Symbols: (○) behenic, (□) stearic, (△) lauric.

### 3.3.2. Adsorption of monocarboxylic acids

In the previous section we concluded that IGC is an appropriate technique for the surface characterization of coated fillers. In this section we compare the adsorption of various surfactants on CaCO$_3$ and the surface characteristics of the coated fillers. We also try to draw conclusions about the effect of the chemical structure of the surfactant
on adsorption and on the arrangement of the surfactant molecules on the surface, i.e. about the structure of the adsorbed layer. In Fig. 3.5 the dispersion component of surface tension is plotted against the amount of surfactant used for the coating of fillers treated with the three linear, saturated carboxylic acids. The character of the correlation is the same in all three cases. However, the minimum appears at different amounts of surfactant; monolayer coverage is reached with less acid as the length of the aliphatic chain increases. This result is in accordance with literature information and indicates that the arrangement, the orientation of the surfactant on the surface of the filler changes with chain length [13]. We assume that at monolayer coverage short chains are oriented vertically to the surface, but with increasing chain length orientation becomes less regular, a single chain occupies a larger area and a looser, less regular structure forms. Naturally, this assumption must be verified by further measurements carried out by appropriate analytical techniques, but this tentative explanation is in accordance both with the experimental results and with published information.

![Figure 3.6](image)

**Figure 3.6** Universal correlation of surface tension and surface coverage. Symbols: (V) oleic, (Δ) lauric, (□) stearic, (○) behenic, (◇) 2-ethylhexanoic acid.

The conclusion drawn in the previous paragraph is further corroborated by Fig. 3.6, in which the dispersion component of surface tension is presented for fillers coated with all the monocarboxylic acids investigated in this study. If the results are plotted on a relative scale, as a function of surface coverage, a single correlation is obtained. The relative scale was created by using the amount of surfactant at which the minimum of surface tension is reached, i.e. we used monolayer coverage as reference value. Although the arrangement of the surfactant molecules on the surface of the filler may
depend on their chemical structure, the surface tension of the filler is the same and depends only on coverage, at least in the case of aliphatic monocarboxylic acids. This result has several important practical consequences. It indicates that surface tension cannot be decreased below a certain minimum value with such compounds. If we want to create weaker filler/filler or filler/matrix interactions, we must use a different approach, compounds with a completely dissimilar composition and/or chemical structure. However, the amount of surfactant needed to reach the minimum depends on the chemical structure of the compound used. This opens up possibilities in the selection of the surfactant, the choice can be based on technological aspects as well as on price/performance relations.

![Figure 3.7](image)

**Figure 3.7** Effect of chain structure on the amount of aliphatic monocarboxylic acids needed for monolayer coverage. Symbols: (□) saturated acids, (▽) oleic, (◇) 2-ethylhexanoic acid.

The influence of the chemical structure of the surfactant is further emphasized by Fig. 3.7, where monolayer coverage determined from surface tension, denoted by \( c_{100} \), is plotted against the chain length of the carboxylic acid used for the treatment. A well-defined linear correlation is obtained for the saturated acids; the amount needed for monolayer coverage decreases with increasing chain length as discussed above. The values obtained for surfactants with a different structure, i.e. with a branch or unsaturation in the molecule, monolayer coverage is reached at lower amounts. This result is again in accordance with literature information [6,8]. A substituent changes the area occupied by the molecule as well as the arrangement of the chains on the surface of the
filler, hinders parallel alignment and creates a looser structure. As we saw above, a looser structure leads to lower surface energy at the same amount of surfactant. Unsaturations have practically the same effect. Double bonds may interact with the surface through induced dipole interaction, which results in the irregular arrangement of the chains on the surface again. These effects offer further possibilities to chose the proper surfactant for the coating of a filler. However, besides price and performance some other factors, like dosing, homogenization and the stability of the compound must be also taken into account by the selection.

![Figure 3.8](image)

**Figure 3.8** Coating of CaCO$_3$ with dicarboxylic acids; effect of the chemical structure and the amount of surfactant used for the treatment. Symbols: (▼) oxalic, (▷) sebacic, (□) stearic acid

### 3.3.3. Adsorption of dicarboxylic acids

The adsorption of dicarboxylic acids is more complicated than that of their monocarboxylic counterparts. They are more polar and the acidic groups situated at both ends of the aliphatic chain offer a variety of possibilities for adsorption. The two groups might be attached to different filler particles, they may be oriented vertically or parallel to the surface or can also form loops. In Fig. 3.8 the changes in the dispersion component of surface tension is plotted against the amount of surfactant used for the treatment for fillers coated with the two dicarboxylic acids. The surface tension of the filler treated with stearic acid is also presented for comparison. Several conclusions can be drawn from the results shown in the figure. A much smaller decrease can be achieved in surface tension if the filler is coated with di- than with monocarboxylic acids. The
changes in the surface characteristics of the filler are negligible when oxalic acid is used and sebacic acid also has only a moderate effect. In the first case the reason of the limited effect is most probably the high polarity of the acid. On the other hand, the longer aliphatic chain of sebacic acid offers more options for the arrangement of the molecule on the surface. It may bite back to the surface, thus both functional groups can take part in the adsorption. However, from the available data, we cannot draw definite conclusions about the arrangement of the surfactant on the filler surface and about the structure of the adsorbed layer, further experiments must be carried out to obtain more information about these questions.

3.4. Conclusions

The study of a CaCO$_3$ filler coated with various mono- and dicarboxylic acids proved that the amount of surfactant which is needed to achieve monolayer coverage can be determined by various techniques, but the most convenient, reliable and universal method is IGC. The dispersion component of surface tension as well as the specific interaction term of the coated filler can be determined from the results, and indirect conclusions can be drawn from them about the orientation of the molecules on the filler surface and the structure of the layer formed. The coverage of the filler with an organic compound leads to a decrease both in the surface tension and in the acid-base character of the filler. In the case of monocarboxylic acids the amount needed for monolayer coverage depends on the chemical structure of the surfactant. Linear chains are assumed to orientated vertically to the surface, and increasing chain length, branches as well as unsaturations lead to a less regular arrangement of the molecules, to a looser structure. However, at the same surface coverage, the surface tension of the filler covered by aliphatic monocarboxylic acids is the same for all compounds. The adsorption of dicarboxylic acids is more complicated and the decrease in surface tension is significantly smaller than for monocarboxylic compounds. Further study has to be carried out to verify the tentative conclusions drawn from IGC results about the orientation of the surfactant and the structure of the layer formed.

3.5. References

19. Ashan, T., Colloid Surfaces 64, 167 (1992)
Chapter 4

Acid-base interactions and interphase formation in particulate filled polymers

4.1. Introduction

Interfacial interactions play an important role in the determination of the properties of all heterogeneous polymer systems including particulate filled polymers [1,2]. These interactions lead to the formation of an interphase with specific properties [3,4], determine the amount of filler which can be added to the polymer (maximum packing fraction) [5], result in the particle size dependence of properties [6,7], and determine the prevailing micromechanical deformation mechanism of the composite [8,9]. The amount of the polymer bonded in the interphase depends on the size of the contact surface between the polymer and the filler, i.e. on the specific surface area of the filler, and on the strength of the interaction. The thickness and properties of the interlayer cannot be measured directly. Spectroscopic methods may indicate the chemical composition of the interlayer or the limited mobility of the bonded chains [10-13], which occasionally can be detected also by dynamic mechanical spectroscopy [14]. Recently atomic force microscopy was used to characterize the interphase in fiber reinforced composites, but the results need further considerations and checking [15,16]. Moreover the use of the technique is rather difficult for particulate filled polymers. As a consequence, indirect methods and modeling are applied for the estimation of interfacial interactions and the thickness of the interphase [5,16].

In particulate filled polymers interfacial adhesion of the polymer matrix and the filler results mostly from secondary, van der Waals forces. Several forces may act between the components including dispersion, dipole-dipole, induced dipole, etc. forces [2,17]. The strength of the interaction is usually estimated by the reversible work of adhesion \( W_d \), which can be determined by one of two approaches. Dispersion forces are taken into account in both, while further interactions occurring in polar systems are described by dipole-dipole interactions in one [18] and by acid-base interactions in the other [18-20]. In an earlier paper we found close correlation between the thickness of the interphase and the reversible work of adhesion calculated from dispersion and dipole-dipole interactions [21]. CaCO\(_3\) was used as filler in that study and it was introduced into neutral and acidic polymers, where significant attraction may develop between the components. However, in basic polymers unfavorable interactions may occur, which might not be described by the approach used earlier.

In this part of our study we wanted to check the effect of specific interactions on interphase formation in particulate filled polymers. Uncoated and surface treated CaCO\(_3\) was introduced both into acidic and basic polymers and the reversible work of adhesion was calculated by both approaches mentioned above. The thickness of the
interphase was deduced from mechanical properties and compared to $W_\text{A}$. The results obtained by the different approaches are discussed in this chapter.

### 4.2. Background

Previous studies proved that the reversible work of adhesion ($W_\text{A}$) gives the best estimate for the strength of interfacial interaction in particulate filled polymers [2,22]. This quantity can be divided into two components: the dispersion and the specific component (Eq. 2.1). According to Fowkes [23,24] the dispersion component of the work of adhesion can be calculated from the dispersion components of surface tension of the polymer and the filler (Eq. 2.2). The first term of Eq. 2.2 is used for the calculation of the dispersion component of $W_\text{A}$ by both theories.

The two approaches differ in the determination of the specific component of the work of adhesion. If we assume that dipole-dipole interactions define adhesion, $W_\text{A}^{sp}$ can be calculated as

$$W_\text{A}^{sp} = W_\text{A}^p = 2 (\gamma_\text{p}^\text{p} \gamma_\text{f}^\text{p})^{1/2}$$  \hspace{1cm} (4.1)

where superscript $p$ indicates the polar component of surface tension. If acid-base interactions develop between the phases, the specific part of the work of adhesion can be determined from the second term of Eq. 2.2 [19,20,25].

The strength of interaction calculated by the two approaches must be compared to its effect, to the thickness of the interphase forming spontaneously in the composite. This quantity can be derived from the mechanical properties of composites by a simple semi-empirical model developed earlier [6,7]. This model expresses the composition dependence of tensile strength in the following way [7]

$$\sigma_T = \sigma_{T0} \lambda^m \frac{1 - \phi}{1 + 2.5 \phi} \exp(B \phi)$$  \hspace{1cm} (4.2)

where $\sigma_T$ and $\sigma_{T0}$ are the true tensile strength of the composite and the matrix, respectively, ($\sigma_T = \sigma \lambda$, where $\sigma$ is the tensile strength), $\lambda$ is relative elongation ($\lambda = L/L_0$, where $L_0$ is gauge length and $L$ the length measured at the moment of failure), $m$ expresses the strain hardening character of the polymer, $\phi$ is the volume fraction of the filler in the composite and $B$ expresses the load bearing capacity of the filler, i.e. it is closely related to interaction. $B$ depends both on the thickness and the strength of the interphase

$$B = (1 + A_f \rho_f \ell) \ln \frac{\sigma_{T}}{\sigma_{T0}}$$  \hspace{1cm} (4.3)
where \( A_f \) and \( \rho_f \) are the specific surface area and density of the filler, \( \ell \) the thickness, while \( \sigma_{ji} \) the strength of the interface. Further details about the model are found elsewhere [6,7,26]. If the tensile strength of the composites is determined as a function of composition, parameter \( B \) can be determined easily. If measurements are done with fillers of the same chemical composition, but different specific surface area, we obtain the thickness of the interphase through Equation 4.3.

### 4.3. Experimental

\( \text{CaCO}_3 \) fillers obtained from various sources were used as fillers in the study. Their most important characteristics are listed in Table 4.1. Low density polyethylene (LDPE) (Tipolen FB 2223, TVK, Hungary), PP (Tipplen H 543F, TVK, Hungary), unplasticized PVC (PVC 5061, BC, Hungary) and polymethyl methacrylate (PMMA) (Diacon APAI., ICI, UK) were used as matrices. Filler content was changed between 0 and 0.3 volume fraction in 0.05 volume fraction steps. The composites were prepared in an internal mixer. Set temperature were 170 °C for LDPE and 190 °C for the other polymers. Homogenization was carried out at 50 rpm for 10 min, then 1 mm thick plates were compression molded from the composites at 170 °C (LDPE) and 190 °C (PP, PVC, PMMA). Tensile bars of 115x10x1 mm dimensions were cut from the plates for further testing.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Abbreviation</th>
<th>Producer</th>
<th>Particle size (µm)</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcilit 100</td>
<td>C100</td>
<td>Alpha Calcit</td>
<td>120.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Millicarb</td>
<td>M</td>
<td>Omya</td>
<td>3.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Omyacarb 2 GU</td>
<td>2GU</td>
<td>Omya</td>
<td>2.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Polcarb</td>
<td>P</td>
<td>ECC (Imerys)</td>
<td>1.3</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The surface tension of the polymers (\( \gamma_p \)) was determined by contact angle measurements. Four liquids were used (\( \alpha \)-bromonaphthalene, water, ethylene glycol, formamide) and both the dispersion and the polar component of \( \gamma_p \) were calculated. The surface tension of the fillers (\( \gamma_f \)) was determined by finite concentration IGC. The dispersion component was derived from adsorption isotherms measured with n-octane, while benzene was used to determine its polar component. The details of the measurement can be found in Ref. 27. The donor and acceptor numbers published by Schreiber [28] were used for the calculation of \( \Delta H^\text{ph} \) and \( W_A \).
The tensile properties of the matrix polymers and the composites were measured at 5 mm/min cross-head speed and 50 mm gauge length using a Zwick 1445 machine. Young’s modulus, yield stress and strain, as well as tensile strength (σ) and elongation-at-break (ε) were derived from measured force vs. elongation traces. Only tensile strength data are presented in this chapter, since they were used for the determination of interphase thickness.

4.4. Results and discussion

The results are presented in three sections. First those obtained on the uncoated filler are reported then the effect of surface treatment on interaction is discussed. The third section compares interphase thicknesses obtained in composites prepared with coated and uncoated fillers and gives a tentative explanation for the observed differences.

![Figure 4.1](image)

**Figure 4.1** Composition dependence of the tensile strength of PMMA/CaCO₃ composites containing fillers with different specific surface area: (O) 0.5 m²/g, (□) 3.6 m²/g, (Δ) 5 m²/g.

4.4.1. Untreated filler

The determination of interphase thickness from tensile yield stress is more reliable than from tensile strength, since the standard deviation of yield stress is smaller
and the strain hardening of the polymer can be neglected. As mentioned before, a close linear correlation was found between $W_A$ and the interphase thickness derived from yield stress in our earlier study [21,22]. Unfortunately, the composites prepared from the polymer, drawn into this study due to its definite basicity, PMMA, fail without yielding, thus tensile strength had to be used for the calculation of interlayer thickness.

Fig. 4.1 shows the composition dependence of tensile strength of PMMA composites prepared with three fillers. The effect of changing specific surface area is clearly seen in the figure. The amount of the polymer bonded in the interlayer increases with increasing $A_f$. The thickness of the interphase is assumed to be the same, since the composites were prepared from CaCO$_3$ and the same polymer in all cases. Parameter $B$ can be derived from the primary data by simple calculations. Reduced tensile strength can be expressed from Eq. 4.2 by eliminating the effect of changing effective load-bearing cross-section of the matrix and the strain-hardening tendency of the polymer.

$$\sigma_{\text{red}} = \frac{\sigma_f}{\lambda^w} \frac{1 + 2.5 \varphi}{1 - \varphi} = \sigma_{r0} \exp (B \varphi)$$  

4.4

![Figure 4.2](image)

**Figure 4.2**  Linear representation of the data of Fig. 4.1 according to Eq. 4.4; effect of specific surface area, (O) 0.5 m$^2$/g, (□) 3.6 m$^2$/g, (△) 5 m$^2$/g.

If we plot the natural logarithm of $\sigma_{\text{red}}$ as a function of filler content a straight line should be obtained with the slope of $B$. The results of Fig. 4.1 are plotted in this way in Fig. 4.2. A very good linear correlation is obtained in each case, parameter $B$ characterizing stress transfer and interaction can be determined with a high accuracy.
The slope is changing with the specific surface area of the filler, as expected.

![Graph showing the relationship between Parameter B and Specific surface area (m²/g)](image)

**Figure 4.3** Determination of interphase thickness by Eq. 4.3 for PMMA/CaCO₃ composites.

**Table 4.2** B values and interlayer thicknesses determined for composites containing uncoated fillers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Parameter B for filler</th>
<th>ℓ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calcilit 100</td>
<td>Omyacarb 2 GU</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.88</td>
<td>2.18</td>
</tr>
<tr>
<td>PE</td>
<td>3.44</td>
<td>6.07</td>
</tr>
<tr>
<td>PP</td>
<td>1.00</td>
<td>1.84</td>
</tr>
<tr>
<td>PVC</td>
<td>1.18</td>
<td>2.87</td>
</tr>
</tbody>
</table>

The thickness of the interphase can be determined from the B values by using Eq. 4.3. According to the equation, B should depend linearly on A_f. The correlation is presented in Fig. 4.3. A straight line is obtained, indeed, proving the validity of the approach. The B values obtained for all combinations of fillers and polymers is compiled in Table 4.2 together with the interphase thicknesses derived from them. The thickest interlayer was obtained for PVC as expected. The interaction of this acidic polymer with the basic filler is strong leading to a thick interphase. Much thinner
interlayer develops in the apolar polymers, in PP and PE. However, the influence of specific interactions cannot be determined from the data of the table unambiguously, we must compare the thickness of the interphase to the strength of the interaction.

The reversible work of adhesion values calculated according to the two approaches presented in a previous section are listed in Table 4.3. $W_A$ is small for the two polyolefins, much larger values were obtained for PMMA and PVC. Attention must be called here to the fact that considerably differing interactions are calculated by the two methods for the two polar polymers. When dipole-dipole interactions are taken into account, the adhesion of PMMA to the filler is stronger than that of PVC, while the latter polymer should adhere better to CaCO$_3$, if acid-base interactions dominate in the composite.

The correlation of interlayer thickness and the reversible work of adhesion is plotted in Fig. 4.4 for the case when we assume that dipole-dipole interactions determine the strength of adhesion and interphase formation. A good linear correlation is obtained for the neutral and acidic polymers just as before [21,22], but the value obtained for PMMA considerably deviates from it. If layer thickness is plotted against $W_A$ calculated from acid-base interactions (Fig. 4.5), all the points, including that of PMMA, fit a general correlation, significant deviation cannot be observed from it. The two figures and the results presented in them clearly prove that in particulate filled polymers acid-base interactions play a significant role in interphase formation thus also in the determination of composite properties. Finally, attention must be called here to the fact that because of the indirect character of the determination of interphase thickness, the obtained result depends on the method used. Dissolution experiments [29,30] and atomistic modeling [31] yielded interlayer thicknesses of a few nanometers, while the use of mechanical properties leads to thicknesses in the micrometer range [32-34], just like in the present case (see Tables 4.2 and 4.5). The range of secondary forces is short, they affect only a small volume (dissolution, modeling), but in the case of large deformations (tensile) a larger volume is involved, because of the decreased mobility of chains attached to the filler surface [2]. Nevertheless, the same factors determine the thickness of the interphase in both cases, as shown by the present chapter.

Table 4.3  Comparison of reversible work of adhesion ($W_A$) values calculated by the two approaches (see Eqs. 2.1, 2.2, 4.1)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Work of adhesion, $W_A$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dipole-dipole</td>
</tr>
<tr>
<td>PP</td>
<td>90.8</td>
</tr>
<tr>
<td>PE</td>
<td>100.8</td>
</tr>
<tr>
<td>PVC</td>
<td>137.7</td>
</tr>
<tr>
<td>PMMA</td>
<td>146.1</td>
</tr>
</tbody>
</table>
Acid-base interactions and interphase formation

Figure 4.4  Correlation of interphase thickness and $W_A$ calculated by considering dipole-dipole interactions.

Figure 4.5  Effect of acid-base interactions on the thickness of the interlayer.
4.4.2. Surface treatment

CaCO₃ fillers are routinely treated with stearic acid to decrease aggregation. The treatment results in decreased interaction with the matrix, i.e. smaller surface tension and work of adhesion [5]. As a consequence, in composites containing the treated filler the role of acid base interaction should decrease compared to those prepared with uncoated CaCO₃ and the interphase should be thinner as well. To check these assumptions fillers were coated with stearic acid and composites were prepared with the coated fillers. The amount of stearic acid was selected to give 100% surface coverage, which was identified as the amount of irreversibly bonded surfactant [2,27,35].

![Figure 4.6](image-url)

**Figure 4.6** Reduced tensile strength plotted against filler content for PP composites prepared with coated fillers of different specific surface area: (□) 0.5 m²/g, (○) 2.2 m²/g, (△) 3.6 m²/g, (▽) 5 m²/g.

The reduced tensile strength of PP composites containing the coated filler is plotted in Fig. 4.6 in the linear representation. Straight lines are obtained again with relatively small deviations, which indicates that the semi-empirical model used for the description of the composition dependence of tensile strength can be used also for composites containing the coated filler. The data presented in the figure demonstrate well also the effect of the specific surface area of the filler. The slope of the straight lines, i.e. parameter B increases with increasing $A_f$. B parameters obtained for the various composites are collected in Table 4.4. In order to help comparison also the values derived for composites containing the uncoated filler are listed in the table. The direct evaluation of the results is rather difficult, far reaching conclusions about
interfacial interactions cannot be drawn from them. We can establish, though, that surface treatment decreases the strength of the interaction, indeed, parameter $B$ is always smaller for the composite containing the treated filler than for the one prepared with uncoated CaCO$_3$.

Table 4.4  *Effect of surface treatment on stress transfer and interaction in particulate filled composites; comparison of coated and uncoated fillers*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Filler</th>
<th>Parameter $B$ for fillers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>uncoated</td>
</tr>
<tr>
<td>PMMA</td>
<td>Calcilit 100</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>Millicarb</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Omyacarb 2 GU</td>
<td>2.18</td>
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<tr>
<td></td>
<td>Polcarb</td>
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</tr>
<tr>
<td>PE</td>
<td>Calcilit 100</td>
<td>3.44</td>
</tr>
<tr>
<td></td>
<td>Millicarb</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Omyacarb 2 GU</td>
<td>6.07</td>
</tr>
<tr>
<td></td>
<td>Polcarb</td>
<td>-</td>
</tr>
<tr>
<td>PP</td>
<td>Calcilit 100</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Millicarb</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Omyacarb 2 GU</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>Polcarb</td>
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<tr>
<td>PVC</td>
<td>Calcilit 100</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>Millicarb</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Omyacarb 2 GU</td>
<td>2.87</td>
</tr>
<tr>
<td></td>
<td>Polcarb</td>
<td>3.37</td>
</tr>
</tbody>
</table>

In order to check the possible effect of acid-base interactions, interphase thicknesses determined for composites containing the coated filler are plotted against the reversible work of adhesion in Fig. 4.7. The strength of interaction, i.e. $W_A$, was calculated by assuming that only dipole-dipole interactions act in the composite. A straight line is obtained with very small deviation from the general tendency; the point obtained for PMMA also fits the line. This proves that the role of acid-base interactions
is much smaller for the treated filler, indeed. We must note here, though, that acceptor and donor numbers are not available for the coated filler, thus $W_A$ calculated from acid-base interactions could not be calculated in order to check the validity of the second approach. These values must be determined in the future in order to verify the conclusions drawn here.

![Figure 4.7](image)

**Figure 4.7** Effect of the strength of interaction on the thickness of the interlayer for composites prepared with coated fillers. Lack of acid-base interactions.

**Table 4.5** Comparison of interphase thicknesses calculated for composites containing uncoated and coated fillers, respectively

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Interphase thickness ($\mu$m) for filler</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>uncoated</td>
</tr>
<tr>
<td>PP</td>
<td>0.117</td>
</tr>
<tr>
<td>PE</td>
<td>0.114</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.175</td>
</tr>
<tr>
<td>PVC</td>
<td>0.226</td>
</tr>
</tbody>
</table>

The results presented in the previous sections corroborated our earlier experience and preliminary assumption that surface treatment leads to a decrease in the
strength of interaction. This conclusion is further supported by Fig. 4.8, where the reduced tensile strength of several composites is plotted as a function of composition in the linear representation. The figure shows that the extent of stress transfer, i.e. interaction, expressed by parameter $B$ depends on the properties of the matrix polymer and on coating. The surface treatment of the filler by stearic acid results in a decrease of surface tension, work of adhesion and parameter $B$, as expected. On the other hand, our other assumption that the thickness of the interlayer also decreases as a consequence of treatment is contradicted by the results shown in Table 4.5. The interphase thickness obtained in the composites containing the treated filler exceeds significantly the values determined with uncoated fillers. This result needs further consideration and explanation.

![Figure 4.8](image)

**Figure 4.8** Influence of matrix properties and surface treatment on the load-bearing capacity of the filler (parameter $B$); (○) PE/uncoated CaCO$_3$, (□) PE/coated filler, (△) PP/uncoated CaCO$_3$, (▽) PP/coated filler. Omyacarb 2GU was used as filler in all four cases.

We may assume that the long aliphatic chain of the fatty acid also take part in the formation of the interlayer. At 100 % surface coverage surfactant molecules are oriented vertically to the surface [22,27] and even its interdiffusion with the matrix might occur. However, if interdiffusion leads to the development of entanglements, it should improve stress transfer, which would lead to increased strength. The results presented in Fig. 4.8 and Table 4.4 strongly contradict this assumption, parameter $B$ always decreased as an effect of surface treatment. Moreover, the stearic acid chain is much shorter than the difference in the thickness of the interlayers determined in the composites containing the two kinds of fillers, thus it cannot contribute to the increased
layer thickness either. Although interdiffusion might occur, it definitely does not lead to the formation of entanglements and improved stress transfer.

Another explanation for the phenomenon may be supplied by the analysis of the simple theory used for the calculation of interphase thickness. Beside the thickness of the interphase, Eq. 4.3 contains other parameters as well. The density of the filler is naturally constant, but the properties of the interlayer may change significantly as an effect of treatment. Because of the weaker interaction and possible interdiffusion, a looser, less stiff interphase may form in composites containing the coated filler. Because of the looser structure and the lower stresses developing in the composite, chains attached to the surface of the filler may have increased deformability thus larger apparent interlayer thicknesses are obtained as a consequence. Naturally, both of the above presented tentative explanations need verification, further study must be carried out to reveal the reason of increased interlayer thickness in the composites containing the treated filler.

4.5. Conclusions

Experiments carried out with polymer matrices of various acid-base characters proved that such interactions play an important role in the development of a spontaneously forming interphase in particulate filled polymers. If the acid-base character of the filler and the polymer is similar, only the consideration of acid-base interactions gives an acceptable estimate of interfacial adhesion. The strength of this latter is determined by the joint effect of dispersion forces and specific interactions. Stronger interfacial adhesion leads to an increase in the thickness of the polymer layer with decreased mobility. The treatment of CaCO₃ with an aliphatic fatty acid decreases the strength of interaction, and changes both the thickness and the properties of the interphase. Acid-base interactions are less important in composites containing coated fillers due to their neutral surface character. In such cases, the consideration of dipole-dipole interactions, which can be easily obtained from infinite concentration IGC measurements, can be also applied for the estimation of interfacial interactions. Further experiments must be carried out to confirm the conclusions presented here. The changes in the thickness and properties of the interlayer as an effect of surface treatment must be studied more in detail as well.

4.6. References

Acid-base interactions and interphase formation

Chapter 5

Morphology and properties of particulate filled polymers

5.1. Introduction

The structure of semi-crystalline polymers, including polypropylene (PP), is relatively complicated. They can crystallize in different modifications, crystallinity and the size as well as size distribution of the crystalline units (lamellae, spherulites) varies in a wide range with changing sample preparation and processing conditions [1-4]. The introduction of a second component into PP usually further modifies morphology. Fillers may act as nucleating agents changing the thermodynamic and kinetic conditions of crystallization [5-8]. Crystal modification, the size of crystalline units and the amount of the crystalline phase may all change as a result [9]. The introduction of particulate fillers often leads to the development of specific morphology; anisotropic particles are usually orientated in different extent [10,11], while spherical fillers frequently form aggregates [12,13].

Because of the considerable number of factors influencing the structure and properties of particulate filled polypropylene, the views concerning their effect are often contradictory. In some cases the direct effect of a certain aspect of crystalline morphology is claimed to determine properties, in others such an influence is denied completely. Hutley and Darlington [14,15], for example, found direct correlation between the crystallization temperature and impact strength of particulate filled PP, while Maiti et al. [16] observed linear dependence of some tensile characteristics on crystallinity. Kendall [17], on the other hand, denied the effect of matrix morphology on composite properties and emphasized the importance of interfacial interaction between the matrix and the dispersed phase.

Talc and CaCO₃ are used in large quantities for the modification of PP [18-20]. The two fillers have different particle geometry and dissimilar effect on the crystalline structure of PP. CaCO₃ consists of more or less spherical particles and influences crystallization only slightly, while talc has plate-like geometry and a strong nucleation effect [9]. The properties of the composites prepared with the two fillers are also different; however, it is still debated whether the changing crystalline structure of the matrix, nucleation, or anisotropy and orientation of the filler cause the observed differences [21]. The goal of this chapter is to give an overview about the factors influencing the properties of particulate filled polymers with special attention to the correlation of structure and properties. Structure-related phenomena occurring in particulate filled polymers are summarized briefly first, then a case study is presented, which shows the effect of various factors acting simultaneously in particulate filled PP and indicating a way how to separate these effects.
5.2. Background

5.2.1. Segregation

The segregation of a second phase during processing was observed in some heterogeneous polymer systems [22,23]. Kubát and Szalánczi [22] investigated the separation of phases during the injection molding of polyethylene and polyamide using the spiral test. The two polymers contained large glass spheres of 50-100 µm particle size and extremely long flow paths up to 1.6 m. They found that considerable segregation took place along the flow path, the glass content of a composite containing 25 wt% filler exceeded 40% locally, at the end of the mold. Occasionally segregation was observed also across the cross-section of the sample; the local amount of filler was larger in the core than at the walls. Segregation depended on filler content and it became more pronounced with increasing size of the particles. Karger and Csikai [23] observed the segregation in elastomer modified PP. They also found an increased amount of the dispersed phase in the center of the specimen.

![Figure 5.1](distribution_of_talc.png)

**Figure 5.1** Distribution of talc across the width of injection molded PP specimens (○) 10 vol%, (□) 20 vol% talc content.

The possible segregation of talc particles dispersed in a PP matrix was investigated in injection molded specimens of 4 x 10 x 150 mm dimensions. Filler content was measured across the cross-section of the specimens by thermogravimetric analysis. As Fig. 5.1 shows, no differences were detected in filler content as a function of position, the particles are homogeneously distributed in the PP matrix independently of average filler content. These and other results indicate that under practical conditions (small
particles, relatively high filler content, normal flow path) segregation is of secondary importance, we may assume the homogeneous distribution of the dispersed phase in the matrix polymer.

5.2.2. Aggregation

Particulate filled composites are produced almost exclusively by the melt mixing of the components, when the shear stresses developing in the processing machine try to separate particles attached to each other [24]. The occurrence and extent of aggregation depend on the relative magnitude of adhesion and separating forces [25-27]. The former is determined by the surface tension of the filler and its particle size, while the latter also depends on particle size as well as on the level of shear forces. As a consequence, aggregation may be decreased by surface treatment, by increasing the particle size of the filler or shear forces [25]. Commercial grades of CaCO$_3$ usually have a wide particle size distribution, thus a fraction of the small particles always aggregates, while large particles are distributed separately. The unambiguous determination of aggregation is difficult; various techniques can be used including measurements carried out on the dry filler, in suspension or on the composite itself [28-33].

Previous results have shown that aggregation always occurs below a certain particle size or above a certain specific surface area [26,27]. In PP composites, the critical value proved to be 5-7 m$^2$/g. Aggregation modifies stiffness only slightly [26], but strength and impact resistance depends very much on structure, both decreases with increasing extent of aggregation [26,27]. The mode of failure initiation depends also on particle size, debonding is the dominating deformation mechanism in composites containing large particles, while cracks are initiated inside aggregates forming at smaller particles sizes [27]. Contradictory results were obtained on the effect of processing technology, injection molded specimens did not always appear to be more homogeneous than compression molded ones [27]. However, a detailed analysis of actual processing conditions and the determination of the number of aggregates proved that properties can be related to the extent of aggregation [34]. On the other hand, deviations from the general tendency indicated that some additional factors also influence properties, which had not been taken into account during the analysis.

One of these factors can be the strength of the aggregates. The strength of agglomerates is of considerable importance in a number of industries, i.e. in granulating of powders, briquetting, pelletizing, etc. As a consequence, several theories were developed for the prediction of agglomerate strength. Manas-Zloczower [35] gives a brief overview about them in a monograph focusing on the mixing and compounding of polymers. Rumpf [36] proposed one of the first equations for the calculation of the tensile strength of aggregates:

\[
T_s = \frac{9}{8} \frac{1 - \varepsilon}{\varepsilon} c F
\]
where $T_s$ is the tensile strength of the aggregate, $d$ is the diameter of the spherical particles in it, $\epsilon_V$ is the volume fraction of voids within the total volume, $c$ is mean coordination number and $F$ mean interparticle force. According to the model the tensile strength of aggregates depends mainly on the particle size of the filler, it increases with decreasing particle diameter. Cheng [37,38] suggested a somewhat different relationship for $T_s$:

$$T_s = \frac{3}{4} H^0 \frac{d \bar{s}}{v} \frac{\rho / \rho_f}{1 - \rho / \rho_f} F^n_{pp}$$

where $H^0$ is the effective surface separation distance of zero tensile strength, $d$, $\bar{s}$, and $v$ are the mean diameter, surface area and volume of the particles, $\rho$ is bulk density and $\rho_f$ the density of the particles, while $F^n_{pp}$ is the interparticle force per unit fracture area.

Kendall [39] strongly criticized the approach of Rumpf [36] and following a completely different approach he proposed a model for aggregate strength, which is based on fracture mechanics:

$$T_s = 15.6 \phi^4 \Gamma_c^{1/6} \Gamma^{1/6} (d c_L)^{1/2}$$

where $\phi$ is the volume fraction of the filler, $\Gamma_c$ the fracture energy of the agglomerate, $\Gamma$ the interfacial energy between particles with a diameter of $d$, and $c_L$ is the length of a macroscopic flaw in the aggregate. The validity of all three models was checked on agglomerated particulate material and good agreement was found between prediction and the experimental results obtained.

Although Manas-Zloczower [35] suggests the use of the same or similar correlation for the prediction of aggregate strength in a polymer matrix, very limited experimental evidence exists to support such an approach. Nevertheless, we may consider the effect of some of the parameters included in Eqs. 5.1 and 5.2 on aggregate strength. The bulk density of the filler can be measured, and according to Eq. 5.2 the tensile strength of the aggregates should become smaller with decreasing bulk density. In Fig. 5.2, the bulk density of 11 CaCO$_3$ fillers [26] with a wide range of particle characteristics is plotted against their specific surface area in logarithmic scale. We can see that with increasing surface area, i.e. decreasing particle size, the bulk density of the filler decreases significantly indicating strongly decreasing tensile strength of the aggregates. The other important parameter, which appears in all equations, is the size of the filler particles. According to Eq. 5.1, the tensile strength of the aggregates is proportional to the reciprocal square of particle diameter. We plotted this quantity as a function of the specific surface area of the fillers in Fig. 5.3. The $1/d^2$ value covers more then 10 orders of magnitude, which indicates that this parameter has a strong influence on aggregate strength, indeed. If Eq. 5.1 is valid, the tensile strength of the aggregates should increase with decreasing particle size drastically.
Figure 5.2  Correlation of the bulk density and specific surface area of various commercial CaCO$_3$ fillers.

Figure 5.3  Dependence of aggregate strength on the particle size of the filler for various CaCO$_3$ fillers.
Unfortunately we cannot check the effect of bulk density and particle size on aggregate strength directly, but we may obtain some information about it from the analysis of composite properties. The tensile strength of PP composites is plotted against filler content in Fig. 5.4. We know that under the effect of external load large particles easily debond from the matrix, which leads to a continuous decrease of tensile strength with increasing filler content. With decreasing particle size the effect of interfacial interactions become more important and tensile strength increases as an effect of the formation of a hard interlayer [25]. At particle sizes smaller than 1.0 \( \mu \)m aggregation becomes noticeable, but the strength of the aggregates is low [27]. However, the tensile strength of composites containing very small particles increases with filler content indicating that debonding is not the dominating deformation mechanism any more. Moreover, the bulk density of this filler is 46 g/l compared to the ~1400 g/l of the largest particles, which proves that Eq. 5.1 predicts aggregate properties better than Eq. 5.2. Although aggregate characteristics must be studied more in detail in the future, aggregate strength may influence composite properties, indeed. We must mention here, though, that PP composites containing 0.001 \( \mu \)m large particles are very stiff and brittle, thus their practical relevance is relatively small.

![Composition dependence of the tensile strength of PP composites containing fillers with different particle size: (○) 0.001 \( \mu \)m, (□) 0.01 \( \mu \)m, (△) 3.6 \( \mu \)m, (◇) 58.0 \( \mu \)m.](image.png)
Figure 5.5  Orientation of talc particles across specimen thickness in injection molded PP composites of different filler content: (○) 10 vol%, (□) 20 vol%.

5.2.3. Orientation

The orientation of anisotropic filler particles occurs in all processing operations and orientation, as well as orientation distribution were shown to influence composite properties drastically. Orientation in extruded and compression molded products is relatively homogeneous, while it changes across the thickness and width of injection molded parts according to the flow pattern developing during mold filling. Several methods are available for the determination of particle orientation, but most of them are rather tedious. ESR spectroscopy proved to be a relatively simple technique, which can be used for the determination of local and average orientation [40,41]. It uses the signal of transitional metal contamination found in every mineral for the determination of orientation. The shape and the intensity of the signal depends on the relative orientation of the crystal planes and the magnetic field and the comparison of the spectrum of the powder and that of the oriented specimens offers a way to estimate the relative orientation of the particles. Further details of the technique can be found elsewhere [40,41]. Fig. 5.5 shows the orientation distribution of talc particles in a specimen of 4 x 10 mm cross-section injection molded from a PP/talc composite of 20 vol% filler content. The distribution agrees well with experience and shows strong parallel orientation of the particles to flow direction at the wall of the mold and their random orientation in the core of the specimen. The strength and stiffness of composites increase considerably parallel to the orientation of anisotropic particles and decrease perpendicular to that [42].
5.2.4. Structure property correlations

The effect of filler content on the tensile strength of particulate filled PP composites are plotted in Fig. 5.6. The composites were injection or compression molded, respectively, and contained CaCO$_3$ or talc particles, i.e. we changed three factors in this series of experiments, filler type, composition and processing technology. The strength of the various composites differs significantly from each other, that of the PP/talc composites of 30 vol% filler content exceeds by far the strength of the material containing CaCO$_3$ in the same amount. As discussed before, several structure related factors may influence the properties of these composites, some are associated with the filler and some with the matrix polymer. The crystal modification of the polymer, the size of the morphological units, crystallinity, as well as the orientation of the crystalline and amorphous phases, all affect the properties of the product. Moreover, all are influenced by processing technology and modified by the strong nucleating effect of talc. The distribution of the filler, homogeneity, aggregation, the anisotropy of filler particles and their orientation, as well as orientation distribution may also play an important role in the determination of composite properties. Naturally more than one factor act simultaneously and the determination of the dominating one is difficult. The possible effect of the various factors is analyzed quantitatively in the following sections and an attempt is made to determine the most important ones.

![Figure 5.6](image-url)

*Figure 5.6  The effect of various parameters on the tensile strength of PP composites; (○,□) CaCO$_3$, (∆,▽) talc.*
5.3. Experimental

Stamylan P16M10 (DSM, The Netherlands) polypropylene homopolymer was used as matrix polymer. Hydrocarb 95 T CaCO$_3$ (Omya, Switzerland, $A_r = 11.0$ m$^2$/g, $d = 1.0$ µm) and Luzenac 10M00S talc (Luzenac, France, $A_r = 8.0$ m$^2$/g, $d = 3.4$ µm) were added to PP to produce the composites processed by injection molding. Different grades of filler were introduced into the composites prepared by compression molding, i.e. Durcal 2 (Omya, Switzerland, $A_r = 3.3$ m$^2$/g, $d = 3.6$ µm) and Finntalc M05 (Finnminerals, Finland, $A_r = 8.4$ m$^2$/g, $d = 2.8$ µm). Composition changed between 0 and 0.3 volume fraction in 0.05 volume fraction steps. Homogenization was carried out using a Brabender DSK 42/7 twin-screw compounder; the blends and composites were cooled in a water bath and pelletized. Specimens were prepared by compression or injection molding, respectively. Tensile testing was carried out at 50 mm/min cross-head speed. Young's modulus (E), yield ($\sigma_y$, $\varepsilon_y$) and ultimate ($\sigma$, $\varepsilon$) properties were determined from recorded force vs. elongation traces. The nucleation effect of fillers and the crystallinity of the composites were studied in the DSC 30 cell of a Mettler TA 3000 Thermal Analysis System. 10 mg samples were measured in two heating and cooling cycles with a rate of 10 °C/min. Relative changes in filler orientation were followed by ESR spectroscopy [21,40,41]. The dispersed structure and orientation of the talc particles were studied by scanning electron microscopy (SEM) on fracture surfaces prepared at liquid nitrogen temperature.

5.4. Results and discussion

5.4.1. Crystalline structure

The nucleation effect of a filler can be deduced from non-isothermal crystallization experiments; the onset of crystallization as well as crystallization peak temperature are related to nucleation and thus to the size of the crystalline units [43,44]. In Fig. 5.7 the crystallization peak temperature of the composites is plotted as a function of composition for injection molded composites. According to the figure talc has a strong nucleating effect, while CaCO$_3$ a much weaker one. The different effect on nucleation and the resulting dissimilarities in crystalline morphology may cause the differences in the properties of talc and CaCO$_3$ filled PP composites, indeed. The crystallinity of the composites prepared with the two fillers shows characteristic differences, too (Fig. 5.8). Crystallinity measured in the first and the second heating cycle, respectively, differs considerably from each other. The first cycle reflects the effect of processing technology, i.e. injection molding in this case, on crystallinity. During the first heating cycle this is completely erased and only the effect of the filler influences crystallinity in the second run. According to the figure the effect of processing technology and the introduction of the filler are completely independent from each other. The orientation of the amorphous and crystalline phases has not been measured, although these might also influence properties.
Figure 5.7  Effect of filler type and content on the crystallization temperature (lamella thickness [43,44]) of PP matrix; (○) CaCO$_3$, (△) talc.

Figure 5.8  Influence of processing technology, filler type and content on the crystallinity of the matrix polymer. Symbols are the same as in Figure 5.7.
5.4.2. Particle related structure

The presence of aggregates was not detected in the composites. The shape of CaCO$_3$ and talc particles differs significantly from each other. Although CaCO$_3$ particles are not spherical, their aspect ratio is close to 1. The anisotropy of talc particles is more significant; their aspect ratio is around 20-30. Although contradictory information is reported on the effect of anisotropy, it certainly influences composite properties. During sample preparation, i.e. processing, orientation of the particles takes place even under the apparently mild shearing conditions of compression molding [21,40]. Both CaCO$_3$ and talc orientates, but the final result is evidently different because of the different aspect ratio of the two fillers. Average values of orientation were measured both in injection molded specimens and compression molded plates by ESR spectroscopy. Relative values related to the sample with the smallest orientation are plotted in Fig. 5.9 as a function of composition. Composition dependence is different, it decreases continuously in the compression molded and exhibits a maximum in the injection molded specimens. The tendency in the composition dependence of orientation indicates that with increasing filler content particles hinder each other in movement, the probability of particle interaction increases. Not only the average orientation, but also its distribution is different in the specimens prepared with the two techniques. Most of the talc particles are oriented parallel to the surface plane of the compression molded plate, while the complicated flow pattern of injection molding leads to a completely different distribution. Particles are oriented parallel to the wall near to it and almost vertically to that in

![Figure 5.9](image-url)
the core of the specimen. It is obvious from these results that the orientation of anisotropic filler particles changes strongly with composition and that these changes may have a pronounced effect on properties.

![Graph showing the reduced strength of particulate filled PP composites plotted against filler content in linear form.](image)

**Figure 5.10** Reduced strength of particulate filled PP composites, plotted against filler content in linear form. (○,□) CaCO₃, (△,▽) talc.

### 5.4.3. Quantitative evaluation

According to Fig. 5.6 the strength of the composites changes both with processing technology and filler type. Talc reinforces PP relative to CaCO₃ and causes even absolute reinforcement for injection molded samples. A decrease of strength is observed as a function of filler content for the compression molded specimens. The composition dependence of strength can be predicted by a simple model, which takes into account the effective load-bearing cross-section of the matrix, the strain hardening of the polymer due to elongation and matrix/filler interaction (Eq. 4.2) [45]. When strength is expressed in reduced, \( \sigma_{\text{red}} = (\sigma_T/\lambda^m) (1 + 2.5\phi)/(1 - \phi) \), or relative, \( \sigma_{\text{rel}} = \sigma_{\text{red}}/\sigma_T \), form, linear correlation of the variables should be obtained as a function of composition in semi-logarithmic plot. Fig. 5.10 shows reduced strength in linear representation. CaCO₃ filled composites correspond to the prediction, they give straight lines with different slopes and intersections. Intersections represent matrix properties, which reflect the dissimilarities in structure resulting from the two processing technologies. It has been shown earlier that \( B \) depends on the size of the interface and the thickness of the interphase (Eq. 4.3.) [46].
The investigated CaCO$_3$ fillers differ both in specific surface area and interaction, since Hydrocarb 95 T was surface treated with stearic acid. It has been shown, however, that specific surface area has a more pronounced effect on the value of $B$ than surface treatment [47,48]. Indeed, composites containing the filler with the larger specific surface area exhibit a steeper slope, in spite of the weaker interfacial interaction in this system.

![Graph showing the relationship between relative tensile strength and volume fraction of filler]

**Figure 5.11** Relative strength of PP/CaCO$_3$ composites, normalized by taking into account the differences in filler characteristics ($B$). (○) injection molded, (□) compression molded.

After taking into account the effect of different specific surface area and interaction of the fillers by normalizing $B$, the relative strength of the CaCO$_3$ filled composites were plotted in the linear form (Fig. 5.11). The two sets of data fall onto the same line proving that the effect of processing technique influences matrix properties independently of the characteristics of the fillers, a factor which was eliminated by calculating relative quantities. The result also shows that the dissimilarity in the properties of the two series of composites filled with the different CaCO$_3$ fillers is caused mainly by the different specific surface area of the fillers and in a lesser extent by different interaction (surface treatment). The independent effect of processing technology and filler characteristics is in agreement with the results of Fig. 5.8, which showed similar composition dependence of crystallinity in the two heating runs. Injection molding changed the absolute amount of crystallinity, but not the tendency implemented by the presence of the filler.
However, the non-linear character of the composition dependence of the composites filled with talc still remains to be explained. In order to take into account the nucleation effect of the talc particles and their orientation, the strength of the composites filled with talc were corrected by a simple approach. Relative crystallinity and orientation were calculated by relating strength measured at each composition to the smallest value determined in each series. Subsequently, composite strength was divided with this relative parameter characterizing structure. Reduced and relative strength values were calculated and plotted in the linear from; the latter correlation is shown in Fig. 5.12. Correction according to crystallinity does not have any effect on strength, it does not change the shape of the correlations presented in Fig. 5.10 and modifies also their position only slightly. However, taking into account average particle orientation results in straight lines. If we plot the natural logarithm of reduced values against composition, the slope and interception of the lines obtained for two set of composites are different again, due to the differences in processing conditions as well as in the orientation distribution of the particles. The effect of talc type can be neglected here, because the particle characteristics (specific surface area, particle size) of the two grades are very similar to each other. These results emphasize again the major role of particle anisotropy, particle orientation and orientation distribution in the determination of composite properties.
5.5. Conclusions

The structure of particulate filled polymers is often more complicated than expected; particles are rarely distributed homogeneously in the matrix. Segregation is usually negligible under practical conditions, but aggregation must always be expected and checked for. The presence of aggregates deteriorates properties, especially impact resistance. Anisotropic particles are always orientated, the extent and direction of orientation determines properties. A case study on the structure and properties of particulate filled PP has shown that composites prepared with CaCO$_3$ and talc have significantly different properties. Tensile strength showed major differences both as a function of particle properties and processing condition. The application of a simple model proved that not the nucleating effect, but the anisometric particle geometry of talc results in its strong reinforcing effect. Processing technology determines the structure of the matrix and the orientation of anisotropic particles; both influence properties significantly. The results obtained prove that the relation between the structure and properties of particulate filled polymers is usually quite complex, practically always several factors influence properties simultaneously.

5.6. References

Chapter 6

Aggregation of particulate fillers: factors, determination, properties

6.1. Introduction

In most cases the structure of particulate filled composites is thought to be very simple, the homogeneous distribution of the particles is assumed in the polymer matrix. However, filler particles may aggregate in such composites leading to problems in processing, to poor aesthetics and to deteriorating properties [1-6]. The understanding of the factors, which influence the aggregation tendency of fillers, offers the only possibility to decrease this phenomenon and to improve composite properties.

Two kinds of interaction exist in particulate filled composites. The polymer adheres to the surface of the particles forming an interphase with properties differing from those of the polymer matrix [7-11], on the one hand, while the particles may also interact with each other creating aggregates [1,3,6], on the other. In the previous chapter we described the main factors determining the extent of aggregation and the way to control it [12-15]. The methods for its determination as well as the difficulties related to it were also mentioned and the corresponding references cited [16-23]. Our previous experiments indicated that a critical size on specific surface area exist for aggregation and we set this value as 5-7 m²/g for PP composites [14,15]. In these experiments contradictory results were obtained concerning the effect of processing; injection molded specimens were not always more homogeneous than compression molded ones [15]. The main goals of this part of our study were the quantitative characterization of the structure of the composites by optical microscopy, comparison the results obtained to mechanical properties and especially to fracture characteristics, and the identification of the most important factors influencing aggregation. An attempt was made to resolve the contradiction concerning the effect of processing technology observed in our earlier study [15].

6.2. Experimental

The trade name and most important characteristics of the fillers used in the study are listed in Table 6.1. Their particle size (d), consequently specific surface area (A_f) covers a wide range leading to very different aggregation tendencies. Besides particle size and specific surface area, their bulk density, sedimentation rate and volume were also determined [14]. An injection molding grade PP homopolymer (Tipplen H 535, MFI = 4 g/10 min at 230 °C, 21.6 N) produced by TVK, Hungary was used for the preparation of the composites, which contained 10, 20 or 30 vol% filler. Two tech-
Aggregation of particulate fillers

Techniques were used for homogenization and sample preparation. A part of the composites were homogenized in a Brabender W 50 EH internal mixer at 190 °C, 50 rpm for 10 min, then compression molded (Fontijne SRA 100) at 190 °C into plates of 1 or 4 mm thickness. Continuous homogenization was carried out in a Brabender DSK 42/7 twin-screw compounder with 190, 200 and 210 °C set temperatures at 50 rpm. The prepared pellets were injection molded into tensile bars of 150x10x4 mm dimensions using a Battenfeld BA 200 CD machine. All further testing was carried out on these bars.

### Table 6.1 Characteristics of the studied fillers

<table>
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<tr>
<th>Filler</th>
<th>Abbreviation</th>
<th>Source</th>
<th>$A_r$ (m²/g)</th>
<th>d (µm)</th>
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</thead>
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<tr>
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<tr>
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<td>Solvay</td>
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<tr>
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<td>0.20</td>
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<tr>
<td>Socal U1</td>
<td>SU1</td>
<td>Solvay</td>
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<td>0.08</td>
</tr>
</tbody>
</table>

The extent of aggregation was characterized by the relative area of aggregates in the composites. Thin slices of 20 µm thickness were cut from the specimens and micrographs were taken from them by a Polaroid digital camera fitted to a Leitz Dialux 20 microscope. The micrographs were quantitatively analyzed by Image-Pro Plus software. Tensile properties, modulus (E), yield stress ($\sigma_y$) and strain ($\epsilon_y$), as well as tensile strength ($\sigma$) and elongation-at-break ($\epsilon$) were measured using a Zwick 1445 apparatus. Modulus was measured at 0.5, while tensile properties at 5 mm/min cross-head speed and 50 mm gauge length. Linear elastic fracture mechanics (LEFM) was used for the characterization of the fracture resistance of the specimens. Instrumented impact testing was carried out at 2.9 m/s velocity; dynamic effects were damped by silicone rubber [24,25]. The specimens of 80 x 10 x 4 mm size were notched to different depths by a saw, then the notch was sharpened by an industrial razor blade to determine strain energy release rate ($G_{1c}$) by the method of Plati and Williams [26,27]. Critical stress intensity factor ($K_{1c}$) was calculated from the maximum force of the recorded load vs. deflection correlations.
6.3. Results and discussion

The results are presented in three sections. First the structure of the composites is analyzed quantitatively as a function of specific surface area, composition and processing technology. The dependence of composite properties on particle size and composition is presented in the subsequent section, then structure-property correlations and the factors determining aggregation are discussed briefly in the final part of the chapter.

6.3.1. Structure

Two micrographs taken from composites prepared by extrusion and injection molding with fillers of different particle sizes are presented in Figs. 6.1a and 6.1b. According to the micrograph shown in Fig. 6.1a large particles of 12 µm size are distributed homogeneously in the polymer matrix, aggregates do not form and cannot be detected in the composite. On the other hand, composites prepared under the same conditions from small particles contain considerable number of aggregates as shown by Fig. 6.1b. These results are in accordance and strongly corroborate our earlier observations that aggregation depends on particle size and its extent increases with increasing specific surface area of the filler [14,15].

According to the previous paragraph, fillers with small particle size has a strong tendency for aggregation. However, the extent of aggregation depends very much also on composition as shown by Fig. 6.2. The micrograph presented in Fig. 6.2a was taken from a composite containing 5 vol% Socal U1 filler. Several large aggregates can be clearly detected in the figure. The number of aggregates and the relative area occupied by them increases with filler content demonstrated well by Fig. 6.2b, which shows a composite containing the same filler, but in a different amount, in 20 vol%.

The relative area of the aggregates determined by image analysis on slices similar to those presented in Figs. 6.1 and 6.2 is plotted against the specific surface area of the fillers in Fig. 6.3. Aggregation becomes stronger with increasing surface area, i.e. with decreasing particle size, but also with composition. Obviously, dispersion becomes more and more difficult as the amount of filler increases in the composite. The tendency, which can be observed as a function of specific surface area is somewhat surprising, though. With decreasing particle size the relative area of aggregates seem to approach a saturation value at all filler contents. One may assume as an explanation that the contact surface between the filler and the polymer increases with increasing $A_f$ leading to larger viscosity, larger friction and less aggregation. This tentative explanation is corroborated by the increasing torque measured during the mixing or extrusion of the composites with decreasing particle size, but further measurements and analysis is needed to prove it unambiguously.
Figure 6.1. Structure of PP/CaCO$_3$ composites prepared by extrusion and injection molding. Filler content: 20 vol%. Particle size: a) 12, b) 0.25 µm.
Figure 6.2a

Figure 6.2b

**Figure 6.2** Effect of composition on the structure of PP/CaCO$_3$ composites. Processing: extrusion/injection molding. Particle size: 0.08 µm. Composition: a) 5, b) 20 vol%. 
Figure 6.3  *Effect of particle size and composition on the extent of aggregation. Extrusion and injection molding. Symbols: (Δ) 5, (□) 10, (○) 20 vol%.*

Figure 6.4  *Structure of a PP/CaCO₃ (0.25 μm, 20 vol%) composite prepared by mixing and compression molding.*
The extent of aggregation is determined by the relative magnitude of adhesion and shear forces prevailing during processing, thus homogenization technology must have a large impact on it. It is generally accepted that in a twin-screw compounding and during injection molding larger shear forces develop in the melt than in an internal mixer or during compression molding. As a consequence, we expected less aggregation and a more homogeneous structure in the composites prepared by the former technology. The micrograph taken from a composite prepared by the second procedure, i.e. internal mixer and compression molding, is presented in Fig. 6.4. The structure of the composite is rather homogeneous, only one medium sized aggregate can be detected in it. If we compare this micrograph to Fig. 6.1b, which was taken from a composite of the same composition, but prepared by extrusion and injection molding, it becomes immediately clear that large differences exist in the homogeneity of the samples. In spite of our expectations, better dispersion is achieved in the internal mixer than in the twin-screw compounder. A plausible explanation is offered by the analysis of the homogenization and sample preparation procedure. Smaller shear stresses developed in the extrusion/injection molding technology, because the twin screw compounder has very deep channels and the relative thick tensile bars were injection molded with a bar gate.

![Figure 6.5](image_url)  
**Figure 6.5** Effect of processing technology on the homogeneity of PP/CaCO₃ composites. Symbols: (O) mixer/compression, (□) extrusion/injection molding.

The effect of processing technology on the structure of the composites can be compared quantitatively in Fig. 6.5, where the relative area of the aggregates is plotted against the specific surface area of the filler. All composites contained 20 vol% filler.
The tendency is the same as in Fig. 6.3. Depending on the intensity of shearing provided by the technology, the filler does not aggregate above a certain particle size and the relative area of aggregates approaches towards a saturation value as a function of specific surface area. The large difference in the efficiency of homogenization is very obvious in the figure, much larger shear forces must develop in the internal mixer than during extrusion and injection molding. The results presented in this section clearly prove that particle size, composition and the relative magnitude of shear forces strongly influence the structure of particulate filled composites. Shear forces are determined by the geometry of the processing equipment and the technological parameters used.

![Figure 6.6](image)

**Figure 6.6** *Effect of particle size on the stiffness of PP composites. Symbols: (Δ) 5, (□) 10, (O) 20 vol%.*

### 6.3.2. Properties

The presence of aggregates influences the various properties of particulate filled composites differently. Modulus usually does not depend very strongly on structure, an experience that is supported also by Fig. 6.6, where the Young’s modulus of the composites is plotted against the specific surface area of the filler. Stiffness increases with filler content as expected, but it is practically independent of $A_f$. This independence can be explained by the low deformations developing during the measurement of modulus.
Figure 6.7  Composition and $A_f$ dependence of tensile yield stress of composites prepared by extrusion and injection molding. Symbols: (△) 5, (□) 10, (○) 20 vol%.

Figure 6.8  Effect of processing technology on the aggregation tendency of CaCO₃ fillers in PP composites at 20 vol% filler content. Symbols: (O) mixer/compression, (□) extrusion/injection molding.
Contrary to stiffness, tensile properties measured at larger deformation change strongly as a function of particle size and they depend also on the degree of aggregation. The tensile yield stress of the composites is plotted against the specific surface area of the fillers in Fig. 6.7. The correlation can be described by two straight lines. Yield stress increases with increasing $A_f$ first, then at a certain value it starts to decrease. The linear dependence of the first section can be explained by a simple theory developed for the description of the composition dependence of yield stress and tensile strength [28,29]. After the critical point the correlation is not necessarily linear, but we do not have enough experimental data in this range to determine the correct function. Yield stress is decreased by aggregation. Large aggregates may behave like large particles, which debonding easily leading to lower yield stress. The strength of aggregates may be also low, they might rupture during deformation with a similar result [33,34]. Quantitative evaluation of the yield stress of the composites offers another approach for the determination of the critical $A_f$ value (or particle size) where considerable aggregation starts at a given processing technology as described in a previous paper [15]. The dependence of tensile strength on particle characteristics and composition is very similar to that of yield stress (see Fig. 6.7) thus we avoid its discussion in order to save space.

![Figure 6.9](image)

**Figure 6.9**  Dependence of fracture toughness on particle characteristics and composition. Extrusion and injection molding. Symbols: (□) 10, (○) 20 vol%.

The effect of processing technology on the tensile strength of the composites is shown in Fig. 6.8. In accordance with the results presented in the previous section, the more homogeneous structure of the composites prepared in the internal mixer leads to better properties, to larger tensile strength. Both the actual strength values and the critical surface area where significant aggregation occurs are larger for these composites.
proving that structure determines properties, indeed. The critical stress intensity factor of the composites depends on particle characteristics and composition in a much more complex way (Fig. 6.9). The very large scatter of the points is not justified by the large standard deviation of the measurement. We should like to call attention here to the experimental value measured at 20 vol% for the filler which has 15 m²/g specific surface area (indicated by a circle). The fracture toughness of the composite containing this filler is much larger than predicted by the general tendency. Obviously, specific surface area does not completely describes the effect of the filler, this single characteristic is unable to predict its aggregation tendency. Strain energy release rate ($G_{k}$) shows an even larger scatter if we plot it as a function of $A_{f}$. Hopefully, the direct comparison of the relative area of aggregates with the mechanical properties and especially with the fracture resistance of the composites yields better correlations and gives us more information about the factors determining the aggregation tendency of particulate fillers.

![Figure 6.10](image)

**Figure 6.10** Correlation between aggregation and fracture resistance. 20 vol%, extrusion and injection molding.

The correlation mentioned at the end of the previous paragraph is presented in Fig. 6.10. The drastic decrease of fracture resistance with increasing extent of aggregation is clear and unambiguous. However, the deviation of several points from the general tendency, especially at large $A_{f}$ values, indicates that similarly to the specific surface area of the filler, the relative area of aggregates is not the sole parameter that determines this property of the composites. Earlier results indicated that several characteristics of the fillers and some properties of the composites depend on $A_{f}$ in a similar way.
Figure 6.11  Correlation of some characteristics of the investigated CaCO$_3$ fillers.

Figure 6.12  Particle size dependence of fracture resistance. 20 vol%, extrusion and injection molding.
For example the bulk density of the fillers is plotted against their specific surface area in Fig. 6.11. A rather close correlation is obtained with the single deviating value of Setacarb OG. Rather surprisingly, the plot of $G_{\text{lc}}$ against $A_r$ resembles very much to the previous correlation, the value of SOG deviates again from the general tendency (Fig. 6.12). Although the scatter of the measured values is larger for $G_{\text{lc}}$ than for bulk density, the tendency is unambiguous as well as the position of the filler mentioned above. These results indicate that the distribution and performance of the filler is determined by the same factors in powder form and in the composite. One factor, which has not been studied yet and might influence properties is the particle size distribution of the filler, which is somewhat different for SOG than for the rest of the fillers. Further study must be carried out in the future to determine its effect on aggregation and on the properties of the composites.

![Figure 6.13](image)

**Figure 6.13**  *Similarity of powder characteristics and composite properties. 20 vol %, extrusion and injection molding.*

To check the correlation of the two quantities, i.e. $G_{\text{lc}}$ and bulk density, they are plotted against each other in Fig. 6.13. A linear correlation is obtained, which indicates that the two quantities are determined by the same or similar factors, indeed. The behavior of Setacarb OG also corresponds to the general tendency. However, three other fillers behave differently, the corresponding values are situated well below the straight line representing the behavior of the majority of the fillers. This result calls attention again to the fact that a single parameter cannot describe the aggregation tendency of particulate fillers and the properties of composites prepared from them. Moreover, although the different particle size distribution of Setacarb HOG may be a convenient explanation for its different behavior, it is still not clear why this difference is not re-
Aggregation of particulate fillers

Reflected in the relative area of aggregates (see Figs. 6.3 and 6.5). Since large aggregates fracture relatively easily and cracks are often initiated inside them [15], their strength might also influence the fracture resistance of the composite [33,34]. However, the low $G_I$ value of the composite containing Omyacarb 15 GU cannot be explained this way, since the large particles of this filler do not form aggregates. The composites containing the three fillers might deform according to different mechanisms than the others, e.g. easier debonding of large particles or aggregates [30,32], but this assumption must be also verified by experiments. Obviously further study must be carried out to identify all the factors, which determine the aggregation tendency of fillers and the properties of particulate filled composites.

6.4. Conclusions

The experiments carried out on PP composites prepared with 11 different CaCO$_3$ fillers proved that most commercial fillers form aggregates under processing conditions used in everyday practice. The extent of aggregation increases with decreasing particle size and increasing filler content. Processing conditions determine the prevailing shear forces thus also the number of aggregates formed. Optical microscopy combined with image analysis is a useful way to characterize the structure of particulate filled polymers, but the relative area of aggregates is not the only factor which determines composite properties. Fillers behave similarly in all media, in bulk, suspension or in the composite. Numerous factors, including the particle size distribution of the filler, influence the extent of aggregation. Composite properties may depend also on the internal structure and strength of the aggregates. Further study must be carried out to identify all the factors determining aggregation and the properties of the composites.

6.5. References

Chapter 7

The mechanism of void formation in particulate filled PE composites

7.1. Introduction

Particulate filled polymers are extensively applied in the automotive industry as bumpers, various panels and structural components, as well as under hood parts [1]. Garden furniture and household articles are also prepared from them and they are applied in construction as well [1,2]. One particular application is the production of breathable films, which allow the passage of vapor, but prevent the permeation of liquids. These films are utilized as the back sheets of diapers, in other sanitary applications and as internal roof insulation [2-4]. In heterogeneous polymer systems, stress concentration develops around the particles under the effect of external load and the actual stress distribution determines the local micromechanical deformation processes [5]. In particulate filled polymers the dominating deformation mechanism is the separation of the matrix/filler interface, i.e. debonding, which leads to a volume increase during deformation [6]. The preparation of breathable films is based on and utilizes this process. Films are produced from polyethylene containing a large amount, 40-50 wt% CaCO₃ and they are stretched to create the porous structure, which makes breathing possible. However, the size of the voids developing during debonding must be controlled otherwise the film does not fulfill its role. Large holes let the liquid also pass through the film, while the moisture vapor transmission (MVTR) of the films is not sufficiently large if only very small voids are created. An optimization of component characteristics and process parameters is necessary to achieve films offering maximum performance, i.e. as large MVTR as possible accompanied by acceptable mechanical properties. Optimization requires the detailed analysis of the debonding process and the factors determining it.

The properties of breathable films depend on the number and size of the voids formed during the deformation. Vapor transmission is determined by their void content, which, on the other hand, depends on the initiation and growth of the voids. The debonding process, which takes place during the deformation of particulate filled polymers, was studied earlier by several authors [7-16]. Models were developed, which predict the conditions for the initiation of debonding [6,17,18], attempts were made to predict the number of debonded particles [8,19] and the growth of voids was also described in a paper [7]. However, a concise analysis of the debonding process has never been carried out in the past. In this part of the work we made an attempt to analyze the separation of matrix/filler interface in polyethylene composites containing various amounts of CaCO₃ filler. Debonding was determined by the measurement of volume increase during deformation and the results were critically analyzed in view of existing theories. The most important factors governing void formation, as well as the number and size of the created particles are pointed out as a result of the analysis.
7.2. Background

The most important characteristic of breathable films is MVTR, which depends on the number and size of voids forming during the stretching process. The initiation of debonding is predicted by models [6, 17, 18], but for ideal conditions. In practice, only a part of the particles initiate the formation of voids, their number must be estimated from measurements with the help of appropriate theories. Finally, the created voids increase during further deformation, their size depends on the extent of stretching and on some other factors [7]. In this section a brief account is given about approaches which can predict the three factors (initiation, number, size) determining the entire debonding process.

7.2.1. Initiation

Two models exist for the prediction of the stress necessary to initiate debonding, those developed by Vollenberg [17,18] and Vörös [20], respectively. According to both models initiation stress depends on the strength of interfacial interaction, on the size of the particles and on the stiffness of the matrix [20], i.e.

\[
\sigma_D = -C_1 \sigma_T + C_2 \sqrt{\frac{W_A E}{R_f}}
\]

where \(\sigma_D\) and \(\sigma_T\) are debonding and thermal stress, respectively, \(W_A\) the reversible work of adhesion, \(E\) the Young’s modulus of the matrix, \(R_f\) the radius of the particles, while \(C_1\) and \(C_2\) are constants. Accordingly initiation stress increases with the interfacial adhesion of the components, with the stiffness of the matrix and with decreasing particle size. The effect of particle size and interfacial adhesion was studied extensively in the past and results unambiguously proved the validity of the model [6,20]. As a consequence, in this chapter, attention is focused on the influence of matrix modulus on the debonding process.

7.2.2. The number of debonded particles

The model leading to Eq. 7.1 was developed by using certain conditions most of which are not fulfilled in practice. Debonding stress was derived for a single particle embedded in an infinite matrix [17,18,20]. However, the particle size distribution of commercial fillers is relatively wide; we cannot expect voids to form around all the particles. According to Eq. 7.1 large particles debond easily, while small ones remain strongly attached to the matrix. The picture is further complicated by the fact that small
particles form aggregates [21-25], which behave as large particles and debond under the
effect of external stress forming very large holes [26]. The number of debonded
particles can be estimated by the measurement of pretrained samples as proposed by
Hartingsveldt [8]. The approach assumes that a part of the filler particles is strongly
bonded to the matrix, carries load and increases stiffness, while the rest debonds and
does not contribute to the increase of modulus. Accordingly, the composition
dependence of Young’s modulus, \( E(\phi) \), can be expressed by the model of Chow [27]:

\[
E(\phi) = \left[ 1 + \frac{\phi_b}{\beta(1-\phi_b)} \right] E_m
\]

7.2

where \( E_m \) is the modulus of the matrix polymer, \( \phi_b \) is the volume fraction of bonded
particles and \( \beta \) takes the form of

\[
\beta = \frac{8 - 10 \nu_m}{15 (1-\nu_m)}
\]

7.3

where \( \nu_m \) is the Poisson’s ratio of the matrix. Since debonded particles do not carry any
load, modulus must be corrected for effective load bearing, i.e.

\[
E_c = \left( 1 - \phi_d^{2/3} \right) E(\phi_b)
\]

7.4

Finally, the following correlation can be written for the relation of the various filler
contents

\[
\phi_b = \phi_f - \phi_d
\]

7.5

where \( \phi_f \) is total filler content, while \( \phi_d \) is the volume fraction of debonded particles. If
we determine the modulus \( E_c \) of pretrained composite samples and know \( \nu_m \), the
amount of bonded \( (\phi_b) \) and debonded \( (\phi_d) \) particles can be calculated from Eqs. 7.4 and
7.5.

7.2.3. Size of the voids

Voids initiated by the separation of the matrix/filler interface grow during
further elongation. Farris [7] carried out his analysis for a single particle and assumed
that each void formed around it is an ellipsoid of revolution with the two equal minor
axes fixed by the diameter of the particle. During deformation the major axis of the void
increases linearly with strain at a rate proportional to the size of the particle contained
by it. Accordingly, the rate of volume increase, thus the size of the formed voids,
depends on filler content in the following way (Eq. 7.6),
\[
\frac{d(\Delta V)}{d\varepsilon_\varphi} = C_F \varphi
\]

where \(\varepsilon_D\) is deformation, \(\varphi\) the volume fraction of the filler and \(C_F\) is a constant. Farris [7] carried out his experiments with cross-linked polyurethane rubbers and claimed that parameter \(C_F\) is close to 1 for particles with uniform size. In subsequent sections we analyze our experimental results by using the models presented above and identify the most important factors which determine the debonding process and finally the MVTR of breathable films.

### 7.3. Experimental

Three polyethylene grades with different stiffness were used in the experiments. Their most important characteristics are listed in Table 7.1. The CaCO\(_3\) filler added to them was Omyacarb 2 GU, the product of Omya GmbH, Switzerland. The average particle size of the filler is 3.6 \(\mu\)m and its specific surface area 3.6 m\(^2\)/g. The filler was used without any coating. Filler content of the composites changed from 0 to 0.3 volume fraction in 0.05 volume fraction steps.

<table>
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<th>Abbreviation</th>
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<th>Producer</th>
<th>MFI (g/10 min)</th>
<th>Density (g/cm(^3))</th>
<th>Modulus (GPa)</th>
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<td>Dow</td>
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<td>0.935</td>
<td>0.4</td>
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<td>TVK</td>
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<td>0.947</td>
<td>0.7</td>
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<td>TVK</td>
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</tr>
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</table>

Composites were homogenized in a Brabender DSK 42/7 twin-screw compounder at 180-190-200 °C and 50 rpm. Injection molded tensile bars of 150x10x4 mm dimensions were produced from the pellets using a Battenfeld BA 200 CD machine. The composites were processed at 160-180-200 °C, the temperature of the mold was kept at 40 °C, while injection pressure was 50 bar, holding pressure 45 bar and holding time 15 sec.

Tensile properties of the composites were derived from force vs. elongation traces recorded by using an Instron 5566 machine with a cross-head speed of 50 mm/min. Volume strain was determined by measuring also the change in one lateral dimension of the specimen by a strain transducer. Volume strain measurements were carried out at 5 mm/min cross-head speed. We assumed that changes in the other lateral direction are the same. In order to determine the number of debonded particles...
The mechanism of void formation in PE composites

specimens were prestrained to different extents. Strained samples were allowed to relax for 15 min and their Young’s modulus was determined at 0.5 mm/min cross-head speed, i.e. 1 % deformation rate. All measurements were done at room temperature.

7.4. Results and Discussion

The various stages of void formation, i.e. debonding and growth are discussed separately in this section. First the main factors determining the initiation of the voids are presented briefly, and then the number of debonded particles is estimated as described above. The rate of void growth and final void content of the composites is discussed in the last subsection.

![Graph](image)

**Figure 7.1** Stress vs. strain and volume strain traces of PE composites containing 20 vol% CaCO₃ filler. ——— PE04, - - - - - - PE07, .............. PE11.

7.4.1. Initiation

The main factors determining the initiation of debonding are specified by Eq. 7.1. The validity of the correlation was proved several times both by Vollenberg [17] and Vörös et al. [6]. Interfacial adhesion and particle size influence debonding stress in
the way described by the model [6]. Less attention was paid to the effect of matrix stiffness. Stress vs. strain, as well as volume strain traces of composites with 20 vol% filler content are presented in Fig. 7.1 for the three polyethylene grades investigated in this study. The stiffness of the matrix polymer strongly influences the modulus, yield stress and yield strain of the composites, the first two decreases, while the last increases with decreasing stiffness, as expected. The differences in volume strain are less unambiguous. The largest volume increase is shown by the softest matrix, while the volume strain of the other two composites is very similar to each other.

![Figure 7.2](image)

**Figure 7.2** Dependence of debonding stress on the stiffness of the matrix (see Eq. 7.1). Symbols: (□) 15 vol%, (○) 20 vol% filler.

Initiation stress ($\sigma_0$) was determined as the intersection of the first, almost horizontal part with the increasing section of the volume strain traces (see Fig. 7.1), and it is plotted against the stiffness of the matrix in Fig. 7.2 in the form indicated by Eq. 7.1. Although only three polymers were included into the study, the correlation presented in Fig. 7.2 strongly supports the model; debonding stress increases linearly with the square root of matrix modulus. Fig. 7.2 supplies an additional proof for the validity of the debonding model developed earlier, thus it could be used for the prediction of the number of voids. Unfortunately, commercial fillers have a wide particle size distribution, which may complicate prediction. Nevertheless, we may assume that besides initiation stress the modulus of the matrix polymer probably influences also the number of debonded particles.
7.4.2. Extent of debonding

Volume strain traces are presented for the softest matrix containing various amounts of filler in Fig. 7.3. It is obvious from the figure that volume increases both with filler content and the extent of elongation. At the largest filler loading the samples broke already after limited extension. Although volume increases with filler content, the extent of debonding cannot be estimated from Fig. 7.3. Comparison of the various traces indicates a nonlinear relationship between volume increase and filler content, which may be caused both by the changing number of debonded particles and the different rate of volume increase. Very small volume increase occurs at low filler content; in fact volume strain could not be measured reliably at 5 vol%. We can conclude, though, that the recorded volume strain traces do not make possible the estimation of the number of debonded particles, this can be determined only by additional experiments.

The modulus of prestrained composite samples is presented in Fig. 7.4. All three matrices contained the filler in 20 vol%. The shape of the correlation is very similar in all three cases, a horizontal or slightly increasing section is followed by a
relatively steep decrease. Modulus seems to reach constant, equilibrium value at large prestrains. The modulus of the three composites differs considerably, and the decrease in stiffness as an effect of prestrain seems to be proportional to the initial modulus of the polymer. The correlations presented in Fig. 7.4 obviously support the validity of Hartingsveldt’s approach [8] assuming that only bonded particles carry load. Nevertheless, the approach merits somewhat more considerations.

![Figure 7.4](image)

**Figure 7.4** Dependence of the modulus of PE composites containing 20 vol% filler on the extent of prestrain. Symbols: (□) PE04, (○) PE07, (△) PE11.

In the investigated composites prepared from a PE and an uncoated filler, interfacial interaction is created by secondary, van der Waals forces. These forces can be characterized by the reversible work of adhesion indicating the reversibility of the debonding process. Although the traces presented in Fig. 7.4 clearly indicate the initiation of debonding, which can be defined as the intersection of the horizontal and the declining sections of the correlations presented in Fig. 7.4, debonding may occur already at smaller deformations. Specimens were allowed to relax for 15 min before the determination of the modulus, during which the interfacial bond could have reformed completely. Several authors, including Vollenberg [17] and Dubnikova [28] claim that initiation occurs in the increasing part of the stress vs. strain curve (see Fig. 7.1), while Pukanszky et al. [6] found that initiation occurs at the maximum of the curve, i.e. at yielding. Although this question cannot be decided here, we may assume that modulus starts to decrease when the specimen was subjected to sufficient prestrain resulting in limited plastic deformation, which prevents the reformation of the original interfacial
bonds. As a consequence, in subsequent sections, we identify the initiation of debonding as the strain at which sufficient plastic deformation occurs, which prevents the reformation of these bonds. These results also imply that debonded particles do not carry load, indeed, and the approach of Hartingsveldt [8] can be used for their estimation.

**Figure 7.5** Effect of prestrain and matrix stiffness on the amount (volume fraction) of debonded filler in PE/CaCO$_3$ composites. (□) PE04, (○) PE07, (△) PE11.

The amount of debonded filler was calculated from the results presented in Fig. 7.4 by the approach mentioned above (see Eqs. 7.2-7.5), and it is plotted against prestrain in Fig. 7.5 for the same composites. The correlation clearly shows the existence of an initiation prestrain, which differs for the three polymers; debonding starts earlier in a stiffer matrix than in a soft polymer. Not only initiation strain or stress, but also the maximum extent of debonded filler differ for the three matrices. The correlations presented in Fig. 7.5 clearly show that in softer matrices only a part of the particles initiate voids, the rest remains bonded to the polymer even at considerably larger deformations than the yield strain of the composite. The character of the correlation and the equilibrium value of the amount of debonded particles indicate that two competitive processes take place during the deformation of these composites: debonding and shear yielding. The relative magnitude of the two determines the number of voids formed and probably also their size. The calculation of relative amounts indicates that more than 90% of the particles debond in the stiffest matrix, while this
number is \( \sim 65 \) and \( \sim 45 \% \) for the other two matrices. This shows that the efficiency of void formation is very poor in the softest matrix, less than the half of the particles contributes to the creation of holes. Moreover, since thin films are deformed under plain stress conditions, which results in large plastic deformation, the efficiency of void formation may be even smaller under the conditions of breathable film production.

![Debonded particles vs. Prestrain](image)

**Figure 7.6** Influence of filler content on the number of debonded particles in PE04/CaCO\(_3\) composites. Symbols: (□) 5 vol\%, (○) 20 vol\%, (△) 25 vol\% filler.

The effect of filler content on the amount of debonded particles is presented in Fig. 7.6 for the softest matrix. At small filler loadings, the determination of this quantity is very difficult, because of the low modulus of the composites and the small changes in properties during prestraining. In spite of these difficulties, the results allow some interesting observations. Debonding is initiated at the same deformation, irrespectively of filler content. Although the absolute amount of debonded particles increases with filler content, the relative amount decreases. According to the results, which might not be very reliable at small filler contents, almost all particles debond at 5 vol\%, while only 40-50 % at larger filler contents. This result requires further investigation and analysis. Aggregates may form at larger filler contents, the decrease of effective load bearing cross-section may increase local plastic deformation and the interacting stress fields of neighboring particles might also influence the extent of debonding. We may conclude that matrix stiffness plays a crucial role in the debonding process of particulate filled polymers and the competition between debonding and shear yielding of the matrix...
determines the actual number of debonded particles. As a consequence, the selection of matrix polymer has a crucial impact on the properties of the breathable films, including MVTR and stiffness.

7.4.3. Size of the voids

The final size of the voids depends on the extent of stretching. According to Farris [7] the rate of volume increase is proportional to the filler content of the composites. He found in his experiments that the proportionality constant, $C_F$, equals 1. Moreover, he investigated cross-linked rubbers, which do not yield and correspond more to the assumptions of his treatment. Conditions are completely different in thermoplastics, where plastic deformation is considerable. These considerations are strongly supported by Fig. 7.7 showing a SEM micrograph taken from the fracture surface of a composite extended to $5\varepsilon_y$ (yield strain). Most of the voids are not regular ellipsoids of revolution and the smaller diameter of the void does not correspond to that of the particle.

![SEM micrograph of voids in PE/CaCO$_3$ composites](image)

**Figure 7.7** Size and shape of voids forming during elongation in PE/CaCO$_3$ composites; $5\varepsilon_y$ strain.
The rate of volume increase, i.e. $d(\Delta V)/d\varepsilon_D$ is plotted against filler content in Fig. 7.8. We obtain three different correlations for the three matrix polymers. All three functions are straight lines, thus corresponding to the prediction of Farris. On the other hand, the slopes of the lines are different from each other and also from 1. The steepest slope was obtained for the softest matrix, while the smallest for PE11. The correlation between parameter $C_F$ and the modulus of the matrix polymer is presented in Fig. 7.9. Obviously, deformation proceeds in a different way in a polyethylene matrix than in a cross-linked rubber. Although three values are not sufficient for drawing unambiguous conclusions, based on Fig. 7.9 we may assume that even further increase in stiffness would not decrease the value of parameter $C_F$ to 1. The large $C_F$ value indicates that much larger voids form in a thermoplastic matrix than in a rubber. This proves again that competitive processes take place during the deformation in the former case and the size of the voids is influenced also by the extent of plastic deformation. Our statement is strongly corroborated by Fig. 7.9, which shows that a $C_F$ value of 3.4 was obtained for the softest matrix, while only 2.5 for the stiffest. Considering the results presented in the previous subsection we may conclude that less particles initiate voids in a soft matrix, but their size becomes larger during further growth than in a stiffer polymer.
**Figure 7.9** Dependence of parameter $C_F$ on the stiffness of the matrix polymer.

**Figure 7.10** Extensive plastic deformation during the deformation of PE04 composites. Effect of filler content and strain on volume increase. Symbols: (□) 5 %, (○) 10 %, (△) 15 %, (▽) 20 % strain.
The influence of plastic deformation on the final void content of the polymer and consequently on permeability is demonstrated well by Fig. 7.10, in which volume increase is presented as a function of filler content at various extents of deformation. At small strains volume does not increase practically at all and at least 0.2 volume fraction of filler is needed to achieve observable volume increase. In accordance with results presented above, only a small fraction of the filler particles debond in the soft matrix and plastic deformation dominates at small filler content. The correlation explains also the uncertainty encountered during the estimation of the number of debonded filler particles at small filler loadings. With increasing filler content the stiffness of the composite as well as the number of voids increase, which result in considerable volume increase. Volume strain is plotted against filler content for the PE07 composites in Fig. 7.11. All correlations are linear showing a proportional increase of void content with increasing filler content, which indicates that plastic deformation is less significant in this polymer than in the softest one. These results prove that all stages of void formation are equally important in the determination of the moisture permeation of breathable films and only the proper optimization of component properties (matrix stiffness, particle size of the filler), composition (filler content) and processing technology (extent and conditions of stretching) may lead to films with acceptable properties.

**Figure 7.11** Volume increase in PE07 composites at different filler contents and deformation. Symbols: (□) 5 %, (○) 10 %, (△) 15 %, (▽) 20 % strain.
7.5. Conclusions

The analysis of the debonding process and the various stages of void formation in particulate filled composites proved that the model developed for the prediction of the initiation of debonding is valid also for the studied PE/CaCO$_3$ composites. Accordingly, debonding stress is determined by the strength of interfacial adhesion, particle size and the stiffness of the matrix. However, in thermoplastic matrices usually two competitive processes take place: debonding and the shear yielding of the polymer. The relative magnitude of the two processes strongly influences the number and size of the voids formed. Because of this competition and due to the wide particle size distribution of commercial fillers, only a fraction of the particles initiate the formation of voids. The number of voids formed is inversely proportional to the stiffness of the matrix polymer. In stiff matrices almost the entire amount of filler separated from the matrix under the effect of external load, while less than 50% debonded in the PE which had an initial modulus of 0.4 GPa. Further decrease of matrix stiffness may lead to the complete lack of debonding and the composite would deform exclusively by shear yielding. Voids initiated by debonding grow during the further deformation of the composite. The size of the voids also depends on the modulus of the matrix. The rate of volume increase considerably exceeds the value predicted for cross-linked rubbers. The results clearly prove that in soft matrices the number of voids is smaller and their size is larger at the same deformation and filler content than in polymers with larger inherent modulus. In order to achieve sufficiently large vapor transmission in breathable films, all parameters of the process must be optimized.

7.6. References

Chapter 8

Summary

The interest of the scientific community in particulate filled composites seemed to decrease with the simultaneous intensification of research on nanocomposites and bio-related materials. Nevertheless, the annual growth in the use of particulate fillers and their composites increases with a higher rate than average economical growth. The interest of the corresponding industry in these materials does not decrease either and new high-tech products appear on the market based on these simple materials. Because of the widespread use and longstanding history of these materials, the factors and correlations ruling their properties are assumed to be known. Constant development activities as well as technological problems indicate that this assumption is false; there is much to be done to obtain sufficient knowledge which makes possible the control of the processing and quality of these materials. This thesis was dedicated to the investigation of some specific questions related to particulate filled polymers, to the characterization of their surface determination of interfacial interactions developing in them, the effect of this latter on the structure of the composites and to micromechanical deformation processes. The subprojects of the PhD work and thus also the chapters of this Thesis are related to each other by the complicated relations among interactions, structure and properties of particulate filled composites. The main goal of the research was always to increase basic knowledge about these questions in order to be able to produce better materials. Although we summarized the most important results of the research at the end of each chapter, we briefly repeat them here to give a concise overview of the achievements of the thesis. At the end of the chapter we summarize the most important new findings of this work.

Linear IGC experiments carried out on a coated and an uncoated CaCO$_3$ filler and the following critical analysis of the results proved that this technique can be successfully used for the surface characterization of fillers and other materials with high energy surfaces. The complete characterization of the filler surface requires the determination of the dispersion component of its surface tension and the knowledge of its acid-base character. Because of the high energy of the surface, it readily adsorbs water thus the parameters measured by IGC depend on column preparation and measurement conditions. Because of the combined effect of conditioning temperature and time, as well as measurement conditions, the determined surface characteristics are not material constants. Different type or grade of fillers, or the effect of coating can be compared only under standard conditions. The use of the same conditioning and measurement temperature eliminates the effect of measurement time. Under appropriate standard conditions the acid-base characteristics of the filler can be determined reliably. However, the accuracy of the determination and the value of the derived parameters depend very much on the selected approach and on the acid-base constants used for the solvent. The enthalpy change of acid-base interaction can be determined the most accurately from measured $\Delta G^{ab}$ values by using the quantity $a_{Li}(f_{Li}^{d})^{1/2}$, which describes the dispersion potential of the probe. The acid-base constants of the filler must be derived from the corrected acceptor number ($AN-AN^d$, $AN^v$) of Riddle and Fowkes and from Gutt-
mann’s donor numbers \( (DN, DN^{**}) \). The results proved that the surface of the CaCO\(_3\) filler used in these experiments is strongly basic in character. Coating significantly reduces basicity. The relatively strong acidic character of the filler coated with larger amount of stearic acid indicates that surface coverage exceeds monolayer coverage and/or the surfactant is distributed unevenly on the filler surface.

The study of a CaCO\(_3\) filler coated with various mono- and dicarboxylic acids proved that the amount of surfactant which is needed to achieve monolayer coverage can be determined by various techniques, but the most convenient, reliable and universal method is IGC. The dispersion component of surface tension as well as the specific interaction term of the coated filler can be determined from the results and indirect conclusions can be drawn from them about the orientation of the molecules on the filler surface and the structure of the layer formed. The coverage of the filler with an organic compound leads to a decrease both in the surface tension and in the acid-base character of the filler. In the case of monocarboxylic acids the amount needed for monolayer coverage depends on the chemical structure of the surfactant. Linear chains are assumed to be orientated vertically to the surface, and increasing chain length, branches as well as unsaturations lead to a less regular arrangement of the molecules, to a looser structure. However, at the same surface coverage, the surface tension of the filler covered by aliphatic monocarboxylic acids is the same for all compounds. The adsorption of dicarboxylic acids is more complicated and the decrease in surface tension is significantly smaller than for monocarboxylic compounds. Further study has to be carried out to verify the tentative conclusions drawn from IGC results about the orientation of the surfactant and the structure of the layer formed.

Experiments carried out with polymer matrices of various acid-base characters proved that such interactions play an important role in the development of a spontaneously forming interphase in particulate filled polymers. If the acid-base character of the filler and the polymer is similar, only the consideration of acid-base interactions gives an acceptable estimate of interfacial adhesion. The strength of this latter is determined by the joint effect of dispersion forces and specific interactions. Stronger interfacial adhesion leads to an increase in the thickness of the polymer layer with decreased mobility. The treatment of CaCO\(_3\) with an aliphatic fatty acid decreases the strength of interaction, and changes both the thickness and the properties of the interphase. Acid-base interactions are less important in composites containing coated fillers due to their neutral surface character. In such cases, the consideration of dipole-dipole interactions, which can be easily obtained from infinite concentration IGC measurements, can be also applied for the estimation of interfacial interactions. Further experiments must be carried out to confirm the conclusions presented in the thesis. The changes in the thickness and properties of the interlayer as an effect of surface treatment must be studied more in detail as well.

The structure of particulate filled polymers is often more complicated than expected; particles are rarely distributed homogeneously in the matrix. Segregation is usually negligible under practical conditions, but aggregation must always be expected and checked for. The presence of aggregates deteriorates properties, especially impact resistance. Anisotropic particles are always orientated, the extent and direction of orien-
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tation determines properties. A case study on the structure and properties of particulate filled PP has shown that composites prepared with CaCO₃ and talc have significantly different properties. Tensile strength showed major differences both as a function of particle properties and processing condition. The application of a simple model proved that not the nucleating effect, but the anisometric particle geometry of talc results in its strong reinforcing effect. Processing technology determines the structure of the matrix and the orientation of anisotropic particles; both influence properties significantly. The results obtained prove that the relation between the structure and properties of particulate filled polymers is usually quite complex, several factors influence properties simultaneously practically always.

The experiments carried out on PP composites prepared with 11 different CaCO₃ fillers proved that most commercial fillers form aggregates under processing conditions used in everyday practice. The extent of aggregation increases with decreasing particle size and increasing filler content. Processing conditions determine the prevailing shear forces thus also the number of aggregates formed. Optical microscopy combined with image analysis is a useful way to characterize the structure of particulate filled polymers, but the relative area of aggregates is not the only factor which determines composite properties. Fillers behave similarly in all media, in bulk, suspension or in the composite. Numerous factors, including the particle size distribution of the filler, influence the extent of aggregation. Composite properties may depend also on the internal structure and strength of the aggregates. Further study must be carried out to identify all the factors determining aggregation and the properties of the composites.

The analysis of the debonding process and the various stages of void formation in particulate filled composites proved that the model developed for the prediction of the initiation of debonding is valid also for the studied PE/CaCO₃ composites. Accordingly, debonding stress is determined by the strength of interfacial adhesion, particle size and the stiffness of the matrix. However, in thermoplastic matrices usually two competitive processes take place: debonding and the shear yielding of the polymer. The relative magnitude of the two processes strongly influences the number and size of the voids formed. Because of this competition and due to the wide particle size distribution of commercial fillers, only a fraction of the particles initiate the formation of voids. The number of voids formed is inversely proportional to the stiffness of the matrix polymer. In stiff matrices almost the entire amount of filler separated from the matrix under the effect of external load, while less then 50 % debonded in the PE which had an initial modulus of 0.4 GPa. Further decrease of matrix stiffness may lead to the complete lack of debonding and the composite would deform exclusively by shear yielding. Voids initiated by debonding grow during the further deformation of the composite. The size of the voids also depends on the modulus of the matrix. The rate of volume increase considerably exceeds the value predicted for cross-linked rubbers. The results clearly prove that in soft matrices the number of voids is smaller and their size is larger at the same deformation and filler content than in polymers with larger inherent modulus. In order to achieve sufficiently large vapor transmission in breathable films, all parameters of the process must be optimized.
The most important conclusions of this thesis can be briefly summarized in the following main points:

1. We proved unambiguously that the determination of the surface characteristics of particulate fillers is difficult because of the adsorption of water by the high energy surface. As a consequence, the determined quantities are not material constants. However, comparison of different type or grade of fillers, or the effect of coating is possible under standard conditions, and we proposed conditions for the characterization of CaCO₃. The use of the same conditioning and measurement temperature eliminates the effect of measurement time.

2. We analyzed the approaches and data available in the literature on the acid-base character of fillers, pointed out the pitfalls of evaluation and proposed the most reliable approach to determine acid-base interactions. The enthalpy change of acid-base interaction can be determined the most accurately from measured $\Delta G_{\text{ab}}$ values by using the quantity $a_i \left( \gamma_L \gamma_i \right)^{1/2}$, which describes the dispersion potential of the probe. The acid-base constants of the filler must be derived from the corrected acceptor number ($AN-AN^d$, $AN^a$) of Riddle and Fowkes and from Guttmann’s donor numbers ($DN$, $DN^{**}$).

3. We showed that the amount of monocarboxylic acids needed for the monolayer coverage of a filler depends on the chemical structure of the surfactant. Linear chains are assumed to be orientated vertically to the surface, and increasing chain length, branches as well as unsaturations lead to a less regular arrangement of the molecules, to a looser structure. We pointed out in the first time that the surface tension of the filler covered by aliphatic monocarboxylic acids is the same for all compounds at the same surface coverage.

4. We proved that only the consideration of acid-base interactions gives an acceptable estimate of interfacial adhesion in particulate filled polymers. We were the first to establish quantitative correlation between the thickness of the polymer layer with decreased mobility and the strength of interfacial adhesion. We also showed that the treatment of CaCO₃ with a surfactant decreases the strength of interaction, and changes both the thickness and the properties of the interphase.

5. We demonstrated that structure-property correlations are extremely complicated in particulate filled polymers having a crystalline matrix. The results indicated that not the nucleating effect, but the anisometric particle geometry of talc results in its strong reinforcing effect. Processing technology determines the structure of the matrix and the orientation of anisotropic particles; both influence properties significantly. We proposed a simple quantitative method which makes possible the separation of the various effects influencing the properties of the composites.

6. It has been known earlier that optical microscopy combined with image analysis is a useful way to characterize the structure of particulate filled polymers. However, we called attention to the fact that the relative area of aggregates is not the only factor which determines composite properties. We proved that fillers behave similarly in all media, in bulk, suspension or in the composite. Numerous factors, including the particle size distribution of the filler, influence the extent of aggregation and composite properties may depend also on the internal structure and strength of the aggregates.
7. We showed that debonding might be the dominating micromechanical deformation process in particulate filled polymers, but in thermoplastic matrices considerable shear yielding of the polymer also takes place. The relative magnitude of the two processes strongly influences the number and size of the voids formed. Because of this competition and due to the wide particle size distribution of commercial fillers, only a fraction of the particles initiate the formation of voids. We proved that in soft matrices the number of voids is smaller and their size is larger at the same deformation and filler content than in polymers with larger inherent modulus.
List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{ch_2}$</td>
<td>Surface area occupied by a –CH$_2$– group (nm$^2$)</td>
</tr>
<tr>
<td>$a_{LV}$</td>
<td>Molecular surface area occupied by adsorbates (nm$^2$)</td>
</tr>
<tr>
<td>$c$</td>
<td>Mean coordination number</td>
</tr>
<tr>
<td>$c_L$</td>
<td>Length of a macroscopic flaw in aggregates</td>
</tr>
<tr>
<td>$c_{100}$</td>
<td>Amount of surfactant needed for monolayer coverage (mmol/100g)</td>
</tr>
<tr>
<td>$c_{100}'$</td>
<td>Monolayer coverage, determiner from surface tension (mmol/100g)</td>
</tr>
<tr>
<td>$d$</td>
<td>Diameter of spherical particles ($\mu$m)</td>
</tr>
<tr>
<td>$\overline{d}$</td>
<td>Mean diameter of particles ($\mu$m)</td>
</tr>
<tr>
<td>$f$</td>
<td>Correction factor for the calculation of the reversible work of adhesion</td>
</tr>
<tr>
<td>$h_{L}$</td>
<td>Ionization potential</td>
</tr>
<tr>
<td>$h_{I}$</td>
<td>Topology index</td>
</tr>
<tr>
<td>$l$</td>
<td>Thickness of the interface ($\mu$m)</td>
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<tr>
<td>$m$</td>
<td>Strain hardening character of polymers</td>
</tr>
<tr>
<td>$n^{ab}$</td>
<td>Number of interacting acid-base sites</td>
</tr>
<tr>
<td>$\bar{s}$</td>
<td>Mean surface area of the particles</td>
</tr>
<tr>
<td>$A_f$</td>
<td>Specific surface area of fillers (m$^2$/g)</td>
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<tr>
<td>$\text{AN}$</td>
<td>Acceptor number</td>
</tr>
<tr>
<td>$\text{AN}^*$</td>
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<tr>
<td>$\text{AN}^{**}$</td>
<td>Normalized acceptor number (kcal/mol)</td>
</tr>
<tr>
<td>$B$</td>
<td>Load bearing capacity of fillers</td>
</tr>
<tr>
<td>$C$</td>
<td>Constant for the determination of the free enthalpy of adsorption</td>
</tr>
<tr>
<td>$C_F$</td>
<td>Proportionality constant of Farris</td>
</tr>
<tr>
<td>$C_1$</td>
<td>Constant for the determination of debonding stress</td>
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<tr>
<td>$C_2$</td>
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<td>$\text{DN}^{**}$</td>
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</tr>
<tr>
<td>$E$</td>
<td>Young's modulus (GPa)</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Young's modulus of composite (GPa)</td>
</tr>
<tr>
<td>$E_m$</td>
<td>Modulus of a matrix polymer (GPa)</td>
</tr>
<tr>
<td>$F$</td>
<td>Mean interparticle force (N)</td>
</tr>
</tbody>
</table>
List of symbols

\( F^o_{\text{pp}} \) \hspace{1cm} \text{Interparticle force per unit fracture area}

\( \Delta G_A \) \hspace{1cm} \text{Free enthalpy change of adsorption (kJ/mol)}

\( \Delta G_A^{ab} \) \hspace{1cm} \text{Acid–base term of the free enthalpy change of adsorption (kJ/mol)}

\( \Delta G_A^d \) \hspace{1cm} \text{Dispersion term of the free enthalpy change of adsorption (kJ/mol)}

\( G_{\text{tc}} \) \hspace{1cm} \text{Critical strain energy release rate (kJ/m}^2\text{)}

\( \Delta G_A^{\text{ab}} \) \hspace{1cm} \text{Enthalpy change related to acid-base interaction (kJ/mol)}

\( H^0 \) \hspace{1cm} \text{Effective surface separation distance of zero tensile strength}

\( K_a \) \hspace{1cm} \text{Constants characterizing the acidity of solid surfaces (kJ/mol)}

\( K_d \) \hspace{1cm} \text{Constants characterizing the basicity of solid surfaces (kJ/mol)}

\( K_a' \) \hspace{1cm} \text{Constants characterizing the acidity of solid surfaces calculated from the free enthalpy of adsorption (kJ/mol)}

\( K_d' \) \hspace{1cm} \text{Constants characterizing the basicity of solid surfaces calculated from the free enthalpy of adsorption (kJ/mol)}

\( K_{\text{tc}} \) \hspace{1cm} \text{Critical stress intensity factor (N/mm}^{3/2}\text{)}

\( L \) \hspace{1cm} \text{Length of the specimen measured at the moment of failure (mm)}

\( L_0 \) \hspace{1cm} \text{Gauge length (mm)}

\( N \) \hspace{1cm} \text{Avogadro’s number (1/mol)}

\( R \) \hspace{1cm} \text{Universal gas constant (J/mol/K)}

\( R^2 \) \hspace{1cm} \text{Accuracy of fitting}

\( R_f \) \hspace{1cm} \text{Radius of spherical particles (\( \mu \text{m} \))}

\( T \) \hspace{1cm} \text{Temperature (K)}

\( T_s \) \hspace{1cm} \text{Tensile strength of aggregates (MPa)}

\( T_b \) \hspace{1cm} \text{Boiling point of solvents (K)}

\( V \) \hspace{1cm} \text{Net retention volume (cm}^3\text{)}

\( V^{\text{ref}} \) \hspace{1cm} \text{Retention volume of a reference solvent (cm}^3\text{)}

\( \Delta V \) \hspace{1cm} \text{Volume increase (cm}^3\text{)}

\( W_A \) \hspace{1cm} \text{Work of adhesion (mJ/m}^2\text{)}

\( W_A^d \) \hspace{1cm} \text{Dispersion term of the work of adhesion (mJ/m}^2\text{)}

\( W_A^p \) \hspace{1cm} \text{Polar term of the work of adhesion (mJ/m}^2\text{)}

\( W_A^{sp} \) \hspace{1cm} \text{Specific term of the work of adhesion (mJ/m}^2\text{)}

\( \alpha_L \) \hspace{1cm} \text{Polarizability of solvents}

\( \beta \) \hspace{1cm} \text{Constant for the calculation of the modulus of composites}

\( \varepsilon \) \hspace{1cm} \text{Elongation at break (\%)}

\( \varepsilon_D \) \hspace{1cm} \text{Deformation}

\( \varepsilon_v \) \hspace{1cm} \text{Volume fraction of voids within the total volume of the aggregate}

\( \varepsilon_y \) \hspace{1cm} \text{Yield strain (\%)}

\( \gamma_{\text{CH}_2} \) \hspace{1cm} \text{Surface tension of polyethylene (mJ/m}^2\text{)}

\( \gamma_f \) \hspace{1cm} \text{Surface tension of the filler (mJ/m}^2\text{)}
### List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma^d )</td>
<td>Dispersion component of surface tension ((\text{mJ}/\text{m}^2))</td>
</tr>
<tr>
<td>( \gamma_{LV}^d )</td>
<td>Dispersion component of the surface tension of a liquid probe ((\text{mJ}/\text{m}^2))</td>
</tr>
<tr>
<td>( \gamma_p )</td>
<td>Surface tension of the polymer ((\text{mJ}/\text{m}^2))</td>
</tr>
<tr>
<td>( \gamma^s )</td>
<td>Dispersion component of the surface tension of adsorbents ((\text{mJ}/\text{m}^2))</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>Interfacial energy between particles</td>
</tr>
<tr>
<td>( \Gamma_c )</td>
<td>Fracture energy of agglomerates</td>
</tr>
<tr>
<td>( \varphi )</td>
<td>Volume fraction of the filler in the composite</td>
</tr>
<tr>
<td>( \varphi_b )</td>
<td>Volume fraction of bonded particles</td>
</tr>
<tr>
<td>( \varphi_d )</td>
<td>Volume fraction of debonded particles</td>
</tr>
<tr>
<td>( \varphi_f )</td>
<td>Total filler content</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Relative elongation</td>
</tr>
<tr>
<td>( \bar{\nu} )</td>
<td>Mean volume of particles ((\mu\text{m}))</td>
</tr>
<tr>
<td>( \nu_m )</td>
<td>Poisson’s ratio of the matrix</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Bulk density of the particles ((\text{g}/\text{l}))</td>
</tr>
<tr>
<td>( \rho_f )</td>
<td>Density of the filler ((\text{g}/\text{cm}^3))</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Tensile strength ((\text{MPa}))</td>
</tr>
<tr>
<td>( \sigma_D )</td>
<td>Debonding stress ((\text{MPa}))</td>
</tr>
<tr>
<td>( \sigma^T )</td>
<td>Thermal stress ((\text{MPa}))</td>
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<tr>
<td>( \sigma_T )</td>
<td>True tensile strength of the composite ((\text{MPa}))</td>
</tr>
<tr>
<td>( \sigma_{T0} )</td>
<td>True tensile strength of the matrix ((\text{MPa}))</td>
</tr>
<tr>
<td>( \sigma_{Ii} )</td>
<td>Strength of the interface ((\text{MPa}))</td>
</tr>
<tr>
<td>( \sigma_{Tred} )</td>
<td>Reduced tensile strength</td>
</tr>
<tr>
<td>( \sigma_{Trel} )</td>
<td>Relative tensile strength</td>
</tr>
<tr>
<td>( \sigma_y )</td>
<td>Yield stress ((\text{MPa}))</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>BMC</td>
<td>Bulk molding compounds</td>
</tr>
<tr>
<td>DEE</td>
<td>Diethylether</td>
</tr>
<tr>
<td>DRIFT</td>
<td>Diffuse reflectance infrared spectroscopy</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EPDM</td>
<td>Ethylene-propylene-diene terpolymer</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
</tr>
<tr>
<td>EtAc</td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>FMC</td>
<td>Flow microcalorimetry</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>IGC</td>
<td>Inverse gas chromatography</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
</tr>
<tr>
<td>LEFM</td>
<td>Linear elastic fracture mechanics</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>MFI</td>
<td>Melt flow index (g/10 min)</td>
</tr>
<tr>
<td>MVTR</td>
<td>Moisture vapor transmission rate</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PA</td>
<td>Polyamide</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>PVC</td>
<td>Polyvinylchloride</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>SIMS</td>
<td>Secondary ion mass spectroscopy</td>
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<tr>
<td>SMC</td>
<td>Sheet molding compound</td>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
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Publications


Conference presentations

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