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PREPARATION OF THERMOPLASTIC POLYMER COMPOSITES USING WATER-ASSISTED TECHNIQUES

THESIS BOOKLET

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1. Introduction

Polymers as engineering materials are widely used for a high variety of applications, due to their low density and acceptable mechanical properties, and because they are simple to prepare. Polymers generally possess a significantly lower stiffness and strength than metals and ceramics. A widely used method to modify their mechanical properties is to incorporate different reinforcing or toughening agents inside the polymers, thus preparing polymer composites. These additives can be of different geometries (fiber, platelet, particle) and of different materials (metals, ceramics and polymers as well). The properties of these composites are affected by the properties of the individual constituents, their ratio within the composite, the strength of the interfacial adhesion between them and also by their dispersion. Their huge benefit compared to single-component materials is that their properties can be well adjusted to the given application by choosing the appropriate amount and type of the constituents. Due to their penetration recently, we can find polymer composites in numerous areas.

The spread of property-tailored polymer composites can be linked with the appearance of glass fiber as composite reinforcement material. It was followed by carbon fiber, aramid, and many other natural and synthetic fibers used as reinforcement. In the last few decades there has been an emerging trend of using micro- and nanosized particles. Their primary function is to modify the properties (mechanical, thermal, electrical, tribological, etc.) of the matrix. Polymer micro- and nanocomposites containing different nanofillers possess outstanding mechanical properties, except toughness. A solution for this issue may be the incorporation of additives (e.g. rubbers) that may enhance the toughness of the matrix as well. Polymers toughened through the dispersion of suitable micro- and nanosized rubber particles are more and more common. The changes in physical properties that can be achieved by the addition of micro- and nanosized fillers can be much more prominent compared to those cases where additives of traditional size are used. The main reason for this is the increasing specific surface area with the decreasing size of the particles. Therefore, the adhesion between the matrix and the additive occurs on a larger surface resulting in a stronger bond. When fabricating polymer composites with micro- and nanoscale additives, the main problem is to achieve a homogenous and fine dispersion of the particles within the polymer matrix.

Micro- and nanosized particles are generally introduced into the matrix in their dry powder form. Since these small particles only started to spread in the last few decades there is no detailed information on their long-term effect on the human body. It is beyond doubt that

these particles, when being inhaled, can get through the airways unimpeded. Depending on their type they can leave the body in a natural way without causing any harm, though there are some that can cause serious damage to human health. The smallest - nanosized - particles may also enter the body unimpeded through its natural boundaries (e.g. through the skin), reaching the bloodstream, cells and nuclei. Health risks can be significantly decreased if these particles are used not in their dry powder form, but dispersed in water before introducing it into the polymer.

Besides the issues with the additives, there is also the matrix as a crucial factor in sustainable development. Up until recently most plastics were derived from petrochemical sources. These classic polymers have a relatively long degradation time, and therefore products manufactured from them are responsible for a huge amount of plastic waste. Public concern about this issue fuels research aimed at developing polymers and additives that are biodegradable and/or derived from renewable resources.

This current research of mine is aimed at the investigation of a novel melt compounding technique, which is suitable to prepare thermoplastic polymer-based composites reinforced and/or toughened with micro- or nanoscale additives. Throughout my work I introduced the reinforcing and toughening agents into the polymer matrix in their aqueous suspension. A significant consideration when choosing matrices and additives was for them to be environmentally friendly if possible. Accordingly, besides petrol-based plastics, I also investigated polymers and additives derived from natural or mineral sources.

2. Summary of the literature, objectives

In the literature review I summarized research in the literature that is related to the processing of polymer micro- and nanocomposites *via* a water-assisted technique. I divided this area of research into two parts, depending on the role of water during processing. In the first group, water acts not only as a medium that helps to achieve a better dispersion of particles, but also as a plasticizer of the polymer matrix. The second group is about polymers, where the water has no other purpose than to help improve the dispersion of additives, therefore it must totally be removed during processing.

The first part of my literature review is about thermoplastic starch (TPS)-based composites reinforced with particles from natural or mineral sources. I revealed how water plays an important role as plasticizer in the processing of starch. I also summarized the changes taking place in the crystalline structure of starch throughout the manufacturing

process. According to the current state of literature, the main drawbacks of TPS are its moisture sensitivity, poor mechanical properties and its significant property change with elapsed time. This latter feature is due to a recrystallization phenomenon, denoted as retrogradation. In recent years, numerous papers have dealt with the enhancement of the properties of TPS using different methods: blending it with biodegradable polyesters, reinforcing it with natural and/or mineral particles, or toughening it with rubber. According to the papers reviewed in my dissertation, rubber-toughening is not a viable option in the case of TPS, due to the differences in the properties of the constituents, even though using rubbers in their latex form could facilitate the use of water-assisted techniques. A promising way, however, is the development of polymer blends (with polyesters) and reinforced composites. Regarding retrogradation, the literature mostly deals with the effect of the plasticizer used. The effect of the reinforcement particles on the initial crystalline structure of thermoplastic starch and its change over time were rarely investigated and when they were, researchers only made rough estimations. Accordingly, the aim of my research is the following:

I.   To investigate the effect of natural and mineral particles - incorporated *via* an aqueous dispersion into the TPS - on TPS.

II.   To investigate the effect of natural and mineral particles on the structure and properties of TPS, over time.

III.   To investigate the properties of TPS/poly(butylene adipate-*co*-terephthalate) (PBAT) blends, and the effect of mineral particles on them. Also, to investigate the effectiveness of the water-assisted technique regarding the dispersion of those mineral reinforcement particles in these samples.

IV.   To reveal how the use of aqueous dispersion facilitates the dispersion of reinforcement particles.

In the second part, I deal with tailoring the properties of the polymer used in highest quantities around the world, polypropylene (PP). According to the literature, it has been researched for decades now. Both reinforcing and toughening PP are thoroughly examined areas. Novel technologies and additives emerging from time to time give new impetus to the development of PP-based materials. Water-assisted melt compounding of polymer nanocomposites is a good example of this, making it possible for researchers to attain a more efficient way to reinforce and/or toughen PP. Likewise, the nanofiller boehmite alumina has great potential as reinforcement but researchers only started to analyze it recently. The aim of

my research is to examine water-assisted melt compounding techniques on PP-based composites, with special emphasis on the following:

      I.   Investigation of the effectiveness of water-assisted techniques during the preparation of rubber-toughened PP samples with respect to the "green approach".

      II.   Investigation of the effectiveness of water-assisted techniques when preparing boehmite alumina-reinforced PP.

3. Materials, preparation methods and characterization

In this section I describe the materials (matrix, reinforcement and toughening agents) used throughout my experiments. The research I conducted can be divided into two major parts: in the first part, I dealt with TPS-based nanocomposites and polymer blends, then in the second part, I prepared and characterized reinforced and rubber-toughened PP samples. The preparation and characterization methods and the parameters set are either the same or may be different in these two sections as the properties of the materials used are very different.

3.1. Materials

3.1.1. Thermoplastic starch-based composites and polymer blends

Native maize starch Hungramid F Meritena 100 (purchased from a local supplier, Brenntag Hungaria Ltd.) with an average particle size of ~5-20 μm was used to prepare the matrix. The food starch used is also suitable for human consumption. As plasticizers for the starch, glycerol (purity of 99.5%) purchased from Csepp Bt., and distilled water were used. Magnesium stearate (MgST) obtained from ICC-Chemol was used for lubrication during melt compounding. Table 1 shows the composition of the thermoplastic starch I prepared based on the literature and my earlier research.

Constituents	Starch	Distilled water	Glycerol	MgST
Amount [m%]	65	17	17	1

Table 1: Composition of the thermoplastic starch prepared

Considering that the matrix in this case is a biopolymer, I chose to use reinforcement particles derived either from natural and/or mineral sources. Accordingly, I used two different types of cellulose and layered silicates for my research. The two types of layered silicates

incorporated as reinforcements were organophilic montmorillonite (type Cloisite 30B obtained from BYK-Gardner GmbH.) and bentonite (type Cloisite 116 also obtained from BYK-Gardner GmbH.). While organo-montmorillonite has a larger intergallery distance due to its modification than bentonite, it is hydrophobic, contrary to bentonite, which is highly hydrophilic. This could lead to differences in their behavior in the case of water-assisted techniques, which I believed was worth investigating.

The most important criterion of choosing cellulose particle types was their size range. Accordingly, two types of microfibrillated cellulose with similar length/diameter ratio were purchased from JRS GmbH.: Arbocel® B 600 (average length ~60 μm, diameter ~20 μm) and the ultrafine Arbocel® UFC-100 (average length ~8 μm, diameter ~2 μm). It is also important that these cellulose particles can be dispersed in water well, therefore the benefits of water-assisted techniques can be exploited.

In order to toughen thermoplastic starch, I used PBAT (type Ecoflex® F Blend C1200) supplied by BASF. Although it is produced from oil-based resources, it is fully biodegradable with the aid of naturally occurring enzymes.

3.1.2. Polypropylene-based composites and polymer blends

I used two polypropylene (PP) types of different molecular weight for my research, both obtained from MOL Petrolkémia Ltd.. One of them was TIPPLEN H 543 F, which is a PP of medium molecular weight. Accordingly, it possesses high enough viscosity for shear forces to occur during that are enough to disperse the additives properly within the matrix. The other type was TIPPLEN H 145 F, which is a PP of low molecular weight, therefore the shear stresses occurring during melt processing were also expected to be lower. The reason for choosing these types was that they have different viscosity ratios when blended with rubber, which should affect dispersion and accordingly, their properties as well. Based on the data sheet, the melt flow rate (MFR) of the former PP according the ISO 1133-1 standard is 4 g/10 mins, while the MFR of the latter is 29 g/10 mins (230 °C / 2.16 kg).

Two different types of uncured rubbers were introduced as toughening agents into PP: a natural rubber (NR) and a carboxylated acrylonitrile butadiene rubber (XNBR). Rubbers were introduced into the PP in their dry and latex form as well. The XNBR latex (Chemigum Latex 550) with 40 wt% solid content was kindly supplied by Omnova Solutions Inc.. The NR latex (G-TEX LATZ) with 60 wt% dry content was obtained from Variachem Kft.. The latter latex was diluted with distilled water for the two lattices to have the same solid content.

Disperal® 40 grade of Sasol GmbH (Hamburg, Germany) was used as boehmite alumina (BA) reinforcement for polypropylene. It is a BA of high purity without any surface modification. The individual ~40 nm particles are present in form of agglomerates (20…80 μm).

Carboxymethyl cellulose, Masstex Pure CMC, an agent used to increase the boiling point of water and to eliminate the Leidenfrost-effect occurring during processing was obtained from Fractal Colors Ltd.. It is a water soluble emulsifier.

3.2. Preparation methods

As the moisture content of starch greatly depends on the temperature and relative humidity of the environment surrounding it, I stored the constituents of thermoplastic starch (starch, reinforcement etc.) under controlled circumstances in order to obtain reproducible results. The materials used were stored in a Memmert HCP153 humidification chamber prior to processing at 30 °C and a relative humidity of 50% for at least 48 h. This step was not necessary for polypropylene-based samples.

Extrusion

The thermoplastic starch was prepared by melt compounding. Before processing, the reinforcement particles used were dispersed in the water, which was also meant to be the plasticizer for the matrix. During the preparation of the samples, neither the bentonite nor the cellulose showed any sign of settling within the water. Subsequently, this dispersion was mixed to the "dry mixture" prepared from all other components (starch, glycerol, MgST). The melt compounding was carried out in a twin-screw extruder (LTE 26–44, Labtech Engineering Co. Ltd.) with an L/D ratio of 44 and a screw diameter of 26 mm. During compounding the temperature of the mixing zones (11 zones) were maintained at 85…120 °C from feed zone to die end. The temperature of the extruder die was 120 °C and the screw speed was set to 75 rpm. The extruder was fed manually to achieve a finer dispersion of reinforcement particles. The extruder barrel was also equipped with an atmospheric vent (in the 8th heating zone) to remove the vaporized water from the melt. The extrudates were pelletized thereafter to pellets of 2 mm length.

Compounding in an internal mixer

The melt compounding of both the TPS-based and the PP-based samples was performed in a batch-type internal mixer, a Brabender Plasti-Corder PL2000, equipped with a kneading chamber of 50 cm^3.

During the compounding of TPS-based samples, the rotor speed was set to 60 1/min and the temperature was set to 130 °C. In the case of samples containing PBAT also, the temperature of the chamber was adjusted to the processing temperature of PBAT, to 140 °C. Information on the melt viscosity of the blends and nanocomposites was obtained from the torque vs. time curves monitored during mixing in the kneading chamber.

In the case of PP samples, compounding was performed at 180 °C with a rotor speed of 60 1/min. The aqueous dispersion of the additives was introduced according to the "fast evaporation compounding" method, introducing the slurry with a syringe dropwise onto the molten polymer. In the case of boehmite alumina - as it was noticably settling within the water - the syringe was shaken at specific intervals for the concentration of the dropped suspension to be as consistent as possible.

Compression molding

Following melt compounding, the blends were then compression molded to sheets of 2 mm thickness in a Teach-Line Platen Press 200E hot press. The TPS-based samples were sheeted at 130 °C (140 °C for samples containing PBAT as well) for 3 minutes, with a pressure of 2 MPa on the surface of the sheets. For polypropylene-based samples, the temperature was set to 200 °C; sheeting also lasted for 3 minutes and the pressure applied was 2.5 MPa. Specimens for testing were either punched or cut out of the compression molded sheets with a Mutronic Diadisk 5200 type cutter.

3.3. Characterization

The TPS-based samples prepared were conditioned at 30 °C and a relative humidity of 50% in a humidification chamber until they were characterized. This step was not necessary for polypropylene-based samples.

Tensile tests

Static mechanical properties were determined by tensile tests, performed on a universal testing machine (Zwick Z005, Ulm, Germany). The TPS-based samples were tested at a crosshead speed of 5 mm/min with specimens type 3, according to EN ISO 8256. The

clamped length was set to 50 mm. The tensile tests of PP-based samples were carried out at a crosshead speed of 25 mm/min with specimens with a length of 100 mm, width of 10 mm and thickness of 2 mm. The tests were performed at room temperature. The average value was derived from five measurements.

Dynamic mechanical analysis

A dynamic mechanical analyzer TA Instruments DMA Q800 was used to assess the thermo-mechanical behavior of the samples. The TPS-based samples were tested in tension mode in the temperature range between -100 and 50 °C. The specimens had a thickness of 2 mm, a width of 4 mm and the clamped length was 10 mm. Prior to the tests, the surface of the specimens was coated with a silicon-based grease to avoid their drying during the test. The PP-based samples were tested in a dual cantilever-type clamp in the temperature range between -50 and 75 °C. The specimens had a thickness of 2 mm, a width of 10 mm and the clamped length was 60 mm. In both cases, the amplitude was set to 0.02% deformation, the frequency was 1 Hz and the heating rate was 3 °C/min.

Charpy tests

Charpy tests were performed on notched specimens (length: 10 mm, thickness: 2 mm) of PP-based samples. The notch length to width ratio of the Charpy specimens was constant, 0.5. The impact test was performed on a Ceast Resil Impactor Junior type instrumented pendulum, equipped with a data acquisition unit (DAS 8000 of Ceast). For the tests a hammer of 2 J impact energy was used. The given test results represent average values of five tests.

Differential scanning calorimetry

The DSC curves were recorded with a TA Instruments DSC Q2000 type calorimeter to examine the thermal behavior of the mixtures. Tests were performed under nitrogen purge with a flow rate of 50 ml/min. The scanning process consisted of three steps: the samples were first heated to 200 °C and kept in a molten state for 5 mins, to erase their thermal history. Then they were cooled from 200 °C to -60 °C at a rate of 10 °C/min, and then heated from -60 °C to 200 °C at 10 °C/min. In the case of PP-based samples, the lower limit of temperature was 0 °C.

Measurement of water uptake

Water uptake was measured with 10 mm x 10 mm x 2 mm specimens. They were weighed immediately after processing and later after different storage durations.

Small angle X-ray scattering

A Siemens D500 diffractometer with a secondary monochromator and CuK_α radiation was used to obtain the diffractograms from which the intergallery distances of layered silicates were calculated. The selected range of the diffraction angle, 2Θ, was between 1° and 10°, the wavelength was $\lambda = 0.15418$ nm. During measurement, the diffraction angle was increased in steps of 0.05°.

Wide angle X-ray scattering

Wide-angle X-ray scattering (WAXS) was used to identify the crystalline structure in TPS and in its BT-reinforced composites. For this test a Philips model PW 3710-based PW 1050 Bragg–Brentano parafocusing goniometer using CuK_α radiation ($\lambda = 0.15418$ nm) was applied. The WAXS scans were recorded for 2Θ angles between 3° and 35°. During measurement the diffraction angle was increased in steps of 0.04°. Crystallinity, and its change over time was determined by subtracting the amorphous halo from the WAXS scans.

Broadband dielectric spectroscopy

The electrical response of the prepared systems was investigated by means of broadband dielectric spectroscopy using an Alpha-N Frequency Response Analyzer (Novamont Technologies) equipped with a dielectric test cell BDS-1200. The voltage amplitude of the applied field was kept constant at 1 V, while the frequency varied from 10^{-1} Hz to 10^6 Hz on 30 °C.

Scanning electron microscopy

The fracture surfaces of the samples were inspected in a scanning electron microscope (SEM; JEOL JSM 6380LA, Tokyo, Japan) using an acceleration voltage of 10…15 kV. Prior to their inspection, the samples were sputter-coated with a gold/palladium alloy.

Atomic force microscopy

Atomic force microscopy (AFM) was used to analyze nanoscale morphology of the bentonite reinforced TPS samples a NanoSurf FlexAFM 5 (Nanosurf AG, Switzerland)

instrument. Phase contrast images were captured in tapping mode with the use of a TAP190 AL-G type cantilever.

Optical microscopy

In order to analyze the macrodispersion of cellulose particles, the polished surfaces of cellulose reinforced TPS composites were inspected in an optical microscope (Olympus BX51M) equipped with a camera CAMEDIA C-5060A.

Particle size distribution within the lattices

A laser diffraction particle analyzer Horiba Partica LA-950V2 was used to determine the initial particle size distribution of the rubber particles in the NR and XNBR lattices.

Determination of viscosity ratio

In case of rubber-toughened PP samples, one of the most prominent factors of the dispersion of rubber particles is the viscosity ratio of the matrix and the elastomer. In order to determine the viscosity of the constituents, I used a MonTech D-RPA 3000 type instrument. Throughout the measurement I set the parameters (temperature, shear rate) so that they represent the conditions within the internal mixer during the compounding process. Accordingly, the measurement was performed at a temperature of 180 °C and a shear rate of 57 1/s. The viscosity ratio was calculated based on the viscosity values determined on the very last second of processing.

4. Theses

1.   The effectiveness of the processing of bentonite-reinforced thermoplastic starch (TPS) composites - where TPS is plasticized with the combination of water and glycerol - depends on the bentonite content. Effectiveness in this case denotes the transformation of the crystalline structure during processing. The reason for this is that the addition of high-stiffness particles increases the shear rate during melt compounding, which leads to a more effective transformation of native starch to TPS. The proportion of native starch specific crystalline structure to the TPS specific crystalline structure decreased monotonously with increasing bentonite content, decreasing from 7% to 4% when 0…7.5 phr bentonite was added. This claim was proved by the results of wide-angle X-ray scattering (WAXS) measurements [1, 2].

2. The rate of retrogradation - where retrogradation is defined as the transformation of crystalline structure throughout the storage time - occurring in TPS plasticized with the combination of water and glycerol decreases if bentonite is introduced as reinforcement. The reason for this is that the presence of these clay particles within the polymer hinders the motion of the chain molecules of the matrix. In a time interval of 120 days, the proportion of the crystalline type specific to native starch that formed as a result of retrogradation decreased from 13% to 6% in TPS-based samples containing 0…7.5 phr bentonite. This claim was proved by the results of wide-angle X-ray scattering (WAXS) measurements. The TPS samples were conditioned at 30 °C, in 50% relative humidity (RH) throughout the entire period [2].

3. In those thermoplastic starch (TPS)-based composites that contain reinforcement particles with a high number of –OH groups, the stiffness-enhancing effectiveness of the reinforcement increases as a function of time. The reason for this is that during storage the matrix reinforcement interphase goes through a change. Because of the retrogradation occurring within the TPS, with time the water content decreases, including the bulk water localized at the matrix reinforcement interphase, which - if being present - could prevent the forming of direct connection between the constituents. With decreasing water content the average number of water molecules that are part of the matrix-reinforcement bonding also decreases, therefore the probability of TPS molecules being bound directly to the reinforcement by H-bonds increases. This claim is proved by the results of mechanical tests and broadband dielectric spectroscopy performed on TPS samples reinforced with cellulose and/or bentonite [2-5].

4. In those thermoplastic starch (TPS)-based layered silicate reinforced composites in which the plasticizers contain enough water to also swell the incorporated layered silicates, the organophilic modification of reinforcing particles before the processing of the composite is not necessary. The reason for this is that in this case, water can have a dual role by not only plasticizing starch but also increasing the intergallery distance of layered silicates to a similar extent that organophilic modification would increase it, thus also facilitating the formation of an intercalated structure.

The claim was proved on TPS samples containing 16.5 wt% water, included in the plasticizer, reinforced with 5 phr of two layered silicates with similar structures: one of those was a hydrophilic type without any organophilic modification, the other one was hydrophobic due to organophilization [6].

5.   The effectiveness of toughening within uncured rubber toughened polypropylene (PP) samples depends not only on the viscosity ratio of the matrix and the uncured rubber introduced as a toughening agent, but also on the way it is introduced into the matrix during melt compounding: in its dry form or as latex. When introduced in the form of latex, the average size of uncured rubber particles within the polypropylene matrix is smaller, therefore the toughening that can be achieved is more effective. The greater the difference in viscosity between the matrix and the uncured rubber is, the greater the increase in toughness is when uncured rubber is used in its latex form.

The claim was proved on PP-based samples of different melt flow indices (4 g/10 mins and 29 g/10 mins according to the ISO 1133-1 standard) toughened with 0…20 wt% natural rubber and carboxylated acrylonitrile butadiene rubber [7, 8].

6.   The size of aggregates within boehmite alumina-reinforced polypropylene composites can be decreased in the case of water-assisted melt mixing methods that do not require the water to be dosaged under high pressure (such as fast evaporation mixing) when introduced into the polymer melt of much higher temperature than the boiling point of water. This can be achieved with the use of a suitable, water soluble agent that can increase the boiling point of water. The increase in boiling temperature has to be enough for the aqueous dispersion to make it into the polymer melt without evaporating on its surface first.

I proved this claim on polypropylene-based composites reinforced with 0…10 wt% boehmite alumina, prepared via fast evaporation mixing. The boiling point of the water was increased by additional carboxymethyl cellulose (CMC) to eliminate the Leidenfrost effect. The weight ratio of CMC and water was 1:40 [9].

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