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**DEVELOPMENT OF CYCLIC BUTYLENE TEREPHTHALATE
(CBT) FILLED RUBBERS**

THESIS BOOKLET

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The review of the thesis and the defence report can be seen in the
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1. Introduction

Elastomers have become widely used engineering materials of our age. This is due to the fact that they are capable of significant reversible deformation, up to several hundred percent, even in the case of low stress, and their strength and other properties can be varied in a wide range if the basic polymer (rubber) and other ingredients are properly selected. Their physical and mechanical properties can be considerably improved with active fillers and reinforcement. Although additives play a key role in determining the properties of the finished rubber, their amount cannot be chosen arbitrarily, since while individual additives improve certain properties, they worsen others. Improving the amount of fillers can lead to problems in processability, and in the case of products of complex geometry and long flow paths, it can lead to incomplete filling of the mould, and a product with missing parts. Therefore, various plasticizers are used in rubber compounds, which reduce viscosity and improve processability but may deteriorate physical and mechanical properties. The issue of compatibility is also very important. The various ingredients of the rubber compound have to be compatible, otherwise the positive effects provided by the individual ingredients cannot be utilized to the fullest. A solution to this problem would be an additive with sufficient compatibility which could reduce the viscosity of the unvulcanised rubber compound but at the same time could improve the mechanical properties, such as the tensile strength and strain at break of the finished, vulcanized rubber.

Cyclic butylene terephthalate oligomer (CBT) is widely used as an additive improving the flowability of thermoplastic polymers. It is also promising in the rubber industry as an additive that can decrease viscosity during processing but hardens during the cooling of the product, and serves as reinforcement. Thanks to its low molecular weight compared to that of polymers, CBT has very low viscosity both at the processing temperature of thermoplastic polymers and at the characteristic moulding and vulcanization temperatures of rubbers. When the finished rubber product cools, it recrystallizes and creates a dispersed reinforcing phase in the final product.

This is the reason why the topic of my PhD thesis is the applicability of CBT as an additive in the rubber industry. One part of my research is the investigation of the effect of CBT on the viscosity of the unvulcanised rubber compound; whether CBT can produce an increase in the flowability of unvulcanised rubber compounds similar to the increase of flowability in the case of thermoplastic polymers. In addition to the characterization of unvulcanised compounds, I investigated the physical properties of the finished vulcanizates.

I also investigated how these effects depend on the properties of the unvulcanised rubber and compounding parameters, such as temperature.

2. Literature review, goals

After a thorough study of the literature, I found that although a large number of studies can be found on CBT and its various areas of application, few papers have been published on the effects of CBT on the various properties of rubber compounds. Research so far has focused on the description of structure, the characterization of polymerization processes, the improvement of the properties of pCBT, and the possible areas of application. In the area of rubbers with CBT as an additive only one type of rubber has been researched (HNBR), but this research focused on the version of CBT capable of polymerization. Some of the results describe the degree of polymerization achievable in these conditions (in the rubber matrix, at the temperature and during the time of vulcanization), and the effect this has on the phase structure. In addition to the description of the effect on mechanical properties, a thorough presentation of the morphological structure can also be found in the literature, along with detailed characterization of the tribological properties of the individual compounds. These include results obtained with various wear test setups, and the possible wear mechanisms are also detailed. These papers, however, do not include the effect of CBT and pCBT on processing, that is, the effect of the oligomer on the viscosity and other parameters of the unvulcanised rubber compound, and the vulcanization properties of the compounds. Studies on CBT so far have almost exclusively focused on a more or less polymerized version of the oligomer, striving to explore its various possibilities. Few references can be found concerning use in the oligomer state, therefore this can also be considered a novel direction of research.

Papers on various new fillers, reinforcing materials and softeners do not provide a comprehensive picture of the effect of the given additive. They usually have one or more traditional fillers, reinforcing materials or plasticizers as reference but the examined properties are not compared to the properties of the unfilled/unplasticized compound. In the case of new fillers and reinforcing materials, research focuses on mechanical and morphological properties, at the expense of processability, while the reverse can be observed in the case of plasticizers (although in their case basic mechanical properties are usually shown).

Based on the above, the goals of my PhD thesis are the following:

- To map the effect of CBT on the processability of unvulcanised rubber compound in the various rubber-based elastomers,
- To find out to what extent CBT can change the mechanical properties of the finished vulcanizates,
- To determine how the effects mentioned in the above two points depend on the properties of the rubber matrix,
- To determine how the effects mentioned above depend on the method of mixing the CBT into the rubber matrix.

3. Materials, and manufacturing and test methods

In this chapter the materials, and manufacturing and test methods are presented briefly.

3.1. Materials

Cyclic butylene terephthalate oligomer

I used cyclic butylene terephthalate oligomer CBT 100 obtained from Cyclics Europe GmbH (Schwarzheide, Germany). It does not contain catalysts and is available in powder format.

Rubbers used

I chose the rubbers that are most often used in the industry. I performed my experiments on natural rubber (NR) and synthetic rubber-based elastomers, and their unvulcanised compounds. I used the following synthetic rubbers: styrene butadiene rubber (SBR), oil-extended styrene butadiene rubber (oSBR), acrylonitrile butadiene rubber with various acrylonitrile contents (NBR), carboxylated acrylonitrile butadiene rubber (NBRX), ethylene propylene diene terpolymer rubber (EPDM), isobutylene isoprene rubber (IIR), and chlorinated isobutylene isoprene rubber (CIIR)

Other materials used

When preparing the rubber mixes, I also used various activators (ZnO and stearic acid), accelerators (CBS, MBTS, ZDBC, TMTD), curing agents (sulphur and dicumyl peroxide), fillers (N330 and N660 carbon black) and plasticizers (paraffinic and naphthenic mineral oil). The recipes of the prepared compounds can be found in the PhD thesis.

3.2. Preparation of compounds and vulcanization

The uncured compounds were prepared with a Labtech Scientific LRM-SC-110 two-roll mill. Mixing was done with a friction of 1.3 (the revolution of the front cylinder was 26 1/min, the revolution of the back cylinder was 20 1/min), and with a gap size of 0.6 mm. The cylinder temperatures during the mixing of CBT into the rubber can be found in the PhD thesis. After the CBT was incorporated, all the rest of the additives and fillers were added at 70 °C. In each case, first the CBT was mixed in, then other fillers and softeners (if any). Then came activators, accelerators and finally, curing agents. The total time of mixing varied between 25 and 30 minutes.

Curing was performed by pressing, for which I used a Collin Teach-Line Platen Press 200E lab press. Curing temperature was 170 °C, while the pressure was 2 MPa. The time was t_{90} , as determined from the vulcanization curves.. The specimens for the tests were cut from the produced 2 mm thick vulcanized sheets.

3.3. Test methods

Investigating vulcanization properties

With a Monsanto vulcameter

The compounds were tested with a MonTech Monsanto R100S (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany) rheometer at a temperature of 170 °C, a frequency of 1.67 Hz, and an amplitude of 3°. Measuring time was 45 minutes.

With a plate-plate rheometer

The vulcanization curves of the compounds were taken with a TA AR2000 (TA Instruments, New Castle, Delaware, USA) parallel-plate oscillation rheometer at a temperature of 170 °C, with an angular frequency of 10 rad/s and a strain amplitude of 1%. Excitation was sinusoidal and the measuring time was 45 minutes.

Viscosity measurements

The viscosity of the oligomer was measured with a TA AR2000 (TA Instruments, New Castle, Delaware, USA) parallel-plate oscillation rheometer between 150 °C and 200 °C at a shear rate of 10 1/s, in plate-plate setup as well.

The absolute value of the complex viscosities of the compounds was measured with a TA AR2000 (TA Instruments, New Castle, Delaware, USA) parallel-plate oscillation rheometer at 170 °C. The angular frequency of the sinusoidal strain was 40 rad/s, while its amplitude was 25%. The individual measurements lasted 3 minutes, during which a value was taken and stored every 3 seconds. Measurement data obtained from the first minute was excluded so that the inhomogeneous temperature distribution of the sample did not influence the measurement results. I calculated the average and the standard deviation of the data obtained in the second and third minutes.

Tensile and tear tests

Tensile tests were performed with a Zwick Z250 (Zwick GmbH, Ulm, Germany) universal tester according to the DIN 53504 standard, on Type 1 specimens of the standard. The load cell was 20 kN, testing speed was 500 mm/min and clamping length was 60 mm. Tear tests were carried out on the same machine, according to the ASTM D624 standard, on type C specimens. Clamping length was 56 mm and testing speed was 500 mm/min. Both tests were performed at room temperature. I further sharpened the tip of the notch of tear test specimens to make sure that the tear definitely occurs at the desired place.

Hardness test

Hardness was tested according to the DIN 53505 standard with a Zwick H04.3150 (Zwick GmbH, Ulm, Germany) hardness tester and with a Shore A head. Hardness was measured in 10 different points in the case of each compound.

DMTA tests

The DMTA tests of the rubber compounds was performed on a TA Q800 (TA Instruments, New Castle, Delaware, USA) DMA, in tensile mode on rectangular specimens cut from the manufactured vulcanized sheets. The nominal dimensions of the specimens were 2.5 mm x 2.0 mm x 10.0 mm (width x thickness x clamping length). Tests were carried out between -100 °C and 100 °C, with a heating rate of 3 °C/min, at a preload force of 0.01 N, a frequency of 10 Hz, and sinusoidal strain amplitude of 0.01% superposed on the strain generated by the preload force.

Scanning electron microscopy (SEM)

I made SEM images of the fracture surfaces of the tensile specimens for the morphological tests of the rubber compounds, with a Jeol JSM-6380LA (Jeol LTD., Tokyo, Japan) scanning electron microscope. To ensure the required conductivity of the specimens for testing, I sputter coated them with a thin gold layer.

DSC tests

DSC tests were carried out on a TA Instruments Q2000 DSC device at a heating speed of 10 °C/min. In the case of the CBT oligomer, the temperature range was -50 °C to 250 °C, while in the case of IIR and CIIR-based compounds, it was between 0 °C and 250 °C.

Oil resistance tests

The NBR-based compound and the EPDM-based compound were subjected to oil resistance tests according to the D471-98 standard.

25 mm x 2 mm x 50 mm (width x thickness x length) specimens were cut from the NBR compound, then immersed in ASTM 3 oil for 70 hours at room temperature. The mass of the specimens before and after immersion was measured and the mass change calculated.

In the case of EPDM-based samples, oil resistance tests were performed similarly to NBR-based samples but the oil used was GM 10w40 semi-synthetic engine oil. In addition to mass change, I also investigated the effect of ageing in oil on mechanical properties with the above-mentioned tensile and tear tests.

4. Theses

I summarized the new scientific knowledge in my PhD thesis in the following theses.

1. Adding cyclic butylene terephthalate (CBT) to unfilled natural and synthetic rubber-based (styrene butadiene, oil-extended styrene butadiene, acrylonitrile butadiene, carboxylated acrylonitrile butadiene, ethylene propylene diene, isobutylene isoprene, and chlorinated isobutylene isoprene), and carbon black-filled natural and synthetic (styrene butadiene and isobutylene isoprene) rubber-based unvulcanised rubber compounds reduces the absolute value of the complex viscosity of the compound in the 150 °C to 170 °C temperature range. This is because in this temperature range CBT is a liquid melt of little dynamic viscosity (19,0±0,8 Pas at 150 °C and 0,8±0,1 Pas at 170 °C), therefore it can operate similarly to oils traditionally used as plasticizers [2, 4, 6, 10].

2. The addition of CBT increases the hardness, tensile Young's modulus, tensile strength, strain at break, and tear strength of styrene butadiene, oil-extended styrene butadiene, acrylonitrile butadiene, carboxylated acrylonitrile butadiene, ethylene propylene diene, isobutylene isoprene, and chlorinated isobutylene isoprene at room temperature, because when CBT hardens during cooling, it acts as a dispersed reinforcing phase in the finished vulcanizate, similarly to conventional fillers [2, 4, 6].

3. The reinforcing effect of CBT on the tensile strength, strain at break and tear strength of vulcanizates at room temperature increases as the frequency of the polar groups in the molecular chain of the base rubber increases. This is because the CBT phase, which is also polar, is dispersed more and more finely, and as the frequency of polar groups increases, the probability of interaction between the polar molecules of the rubber and the CBT phase also increases [2, 4].

4. The temperature at which the CBT is mixed in influences its reinforcing potential. At higher compounding temperatures (120°C), the specific area of the CBT phase increases in the case of both apolar SBR and polar NBR-based compounds. In the case of SBR, it is because the particles constituting the CBT phase become finer, while in the case of NBR, the shape of the crystals of the CBT phase changes [3].

5. List of publications

5.1. Foreign language peer-reviewed articles

1. **Halász I.Z.**, Romhány G., Kmetty Á., Bárány T., Czigány T.: Failure of compression molded all-polyolefin composites studied by acoustic emission, *Express Polymer Letters*, 9, 321-328 (2015) **IF=2,935**
2. **Halász I.Z.**, Bárány T.: Novel bifunctional additive for rubbers: cyclic butylene terephthalate oligomer. *Periodica Polytechnica Mechanical Engineering*, 59, 182-188 (2015).
3. **Halász I.Z.**, Bárány T.: Phase morphology and mechanical properties of cyclic butylene terephthalate oligomer-containing rubbers: effect of mixing temperature. *Materials*, 9 (2016). **IF=2,728**
4. **Halász I.Z.**, Bárány T.: Effect of Cyclic Cutylene Terephthalate Oligomer on the Properties of Styrene-Butadiene and Acrylonitrile-Butadiene Rubbers, *Periodica Polytechnica Chemical Engineering*, **IF=0,460 submitted**

5.2. Publications in Hungarian

5. **Halász I.**: Ciklikus butilén-tereftalát – mint polimer alapanyag és polimer adalékanyag, *Műanyagipari Szemle*, 10, 76-80 (2013)
6. **Halász I.**, Bárány T.: Elasztomerek tulajdonságainak újszerű módosítási lehetősége, *Műanyag és Gumi*, 51, 315-318 (2014)
7. **Halász I.**, Hajdu S. M., Bárány T., Karger-Kocsis J.: Újfajta nanoerősítőanyagokkal töltött elasztomer-mátrixú nanokompozitok, *Polimerek*, 2, 170-174 (2016)

5.3. Conference-related publications

8. **Halász I.**, Bárány T., Karger-Kocsis J.: Effect of cyclic butylene terephthalate (CBT) oligomer on the processability and mechanical properties of thermoplastic polyester elastomer, *Mechanical Engineering Conference 2012, Proceedings* 172-179 (2012)
9. **Halász I.**, Bárány T.: Styrene-butadiene rubber/graphene nanocomposites: Effect of co-milling with cyclic butylene-terephthalate, *Materials Science Forum*, 812, 65-70 (2015)
10. **Halász I.**, Bárány T., Karger-Kocsis J.: Effect of cyclic butylene-terephthalate on carbon black filled rubbers , *International Rubber Conference, Nuremberg, Germany* (2015)