UNIVERSITY OF PANNONIA

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MSc in Chemical Engineering

IMPACT ASSESSMENT OF OLEFIN-MALEIC-ANHYDRIDE BASED COMPATIBILIZING ADDITIVES IN WASTE ELASTOMER CONTAINING POLYMERS

Theses of PhD dissertation

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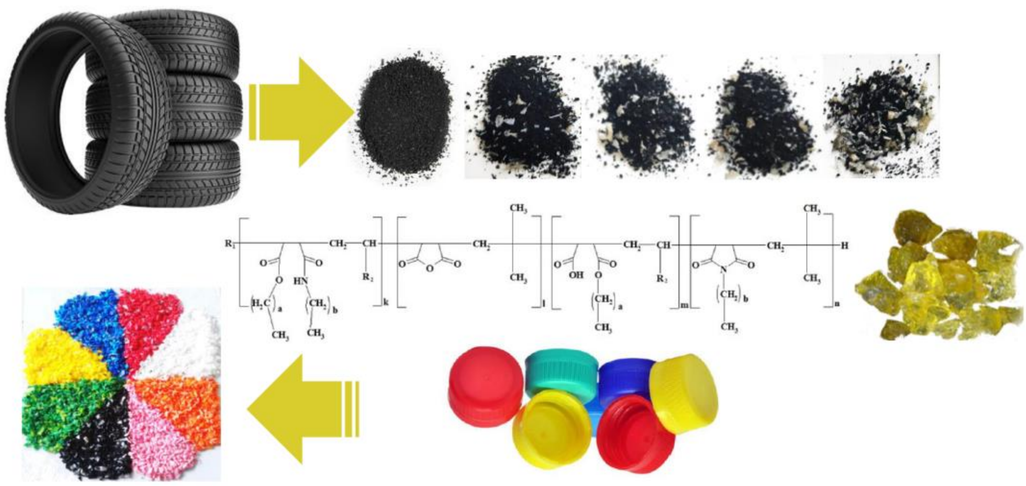

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1. Introduction

There is a growing need for recycling of waste tyre rubbers as a consequence of increasing demand for tyre rubbers and their continuous wearing. Appearing of new components in tyre formulations is permanent as the result of new manufacturing technologies making the recycling more complicated. Since the tyre rubbers consist of not only natural and synthetic rubbers i.e. conventional elastomers, but also new components in relatively high ratios compared to the previous types, thereby, recovery of the unique components is much more complex.

Discarded tyre rubbers were sometimes stored in stockpiles or they were landfilled until the turn of the millennium. Stockpiled tyre rubbers have led on the one hand to the contamination of the soil and on the other hand to the formation of ecosystems which serve as substrates for animals like mosquitoes and rats. Since tyre rubbers are combustible they can be the source of uncontrolled fires, unfortunately even today. Planned and controlled incineration of the accumulated tyre rubber stocks can last for months and give rise to health and environmental problems. Landfilled tyre rubbers also cause serious health and environmental damage through the contamination of soil and ground-water. The European Committee prohibited the stockpiling of waste tyre rubbers in landfills based on the Council Directive of 1999/31/EC in order to reduce the aforementioned risks. Solutions for rubber recycling have mainly been developed in the recent twenty years and newer solutions allow recycling even in higher quantity as the result of continuous development.

Rubber is characterized by a cross-linked structure having no reactive functional groups on the surface and it does not melt in the classical sense consequently its compatibility is really low with other materials, like polymers. Incorporation of ground tyre rubber into a polymer matrix provides an advantageous opportunity within the methods of mechanical recycling. Application of compatibilizing additive is essential to improve the compatibility between the phases. These compatibilizers decrease interfacial tension between the phases, thereby, micromechanical deformation and cavitation can be reduced and size of the agglomeration formed by rubber particles can be minimized. These types of additives play the role of wetting agents supporting the propagation of stress, which manifested itself through the improvement of mechanical properties of the blend.

It can be stated generally that main requirements of the effective waste management are accessibility of raw materials in large amounts and in relatively homogenous quality having low contaminant content. These conditions can be fulfilled no way by the wide variety of waste elastomers and even waste polyolefins can meet the aforementioned requirements only partially. Right direction of recycling can not be appointed exactly, since several types of waste material originated from different sources have to be recycled, furthermore, the number of feasible combinations of waste elastomer/polymer are high. These are the reasons why no universal solution exists in the waste management.

2. Objectives

Main aim of the research work has not been to develop a new material or a new recycling method but to optimize mainly waste polyolefin and waste elastomer based systems useful for industrial practice meanwhile satisfying requirements of sustainability. Development a flexible system consisting of correlations and measurement methods has been defined as a goal managing easier selection of the appropriate composition of the waste elastomer/polyolefin blend based on the available and determinative properties of the waste raw material even with a definite range of quality changes. Compatibility of the blends from mainly waste elastomer and polymer phases has been planned to improve with addition of experimental compatibilizing additives in a controlled way considering that each waste material based system is unique and therefore requires optimization. It means that proper selection of the ratio of functional groups (half-ester, anhydride, ester amide, imide) in the compatibilizing additive results in improved mechanical properties achieved by intensified interfacial interaction between the phases and that can be connected with structural properties of the additives and blends derived from FT-IR, oscillatory rheometry or morphology.

Determination of optimal processing time and conditions have been aimed at before addition of additives to polyolefin or blends. Influencing role of blend composition, type of the elastomer, its particle size and distribution have also been studied for exact identification of effects originated from the additive structure.

Examination of applicability of oscillatory rheometry and exploring contexts to mechanical properties of the blends has been mentioned also among the aims, since general rules and contexts are not directly applicable for a dispersed system i.e. for polymer melts containing waste elastomers. Introduction of experimental compatibilizing additives appears as an extra factor during evaluation of the results achieved by oscillatory rheometry considering waste elastomer/polymer systems. Therefore, identifying structural effects of the compatibilizing additives by oscillatory rheometry has also been considered as a goal.

3. Methods

- For classification of materials
    - Titrimetry (determination of acid and saponification number)
    - Particle size analysis
    - Inverse gas chromatography
    - Gel permeation chromatography
    - Scanning electron microscopy
    - FT-IR spectroscopy
    - Oscillatory rheometry

- For examination of polymers/blends
    - Determination of tensile properties
    - Determination of Charpy impact strength
    - Determination of melt flow index
    - Scanning electron microscopy
    - FT-IR spectroscopy
    - Oscillatory rheometry

4. New scientific results

1. Based on extending classical mechanical measurements of polymers with up-to-date ones such as oscillatory rheometry, SEM and FT-IR analysis in waste HDPE processed by two-roll mill property modifying effect of the olefin-maleic-anhydride copolymer based additives has been stated to be influenced by the ratio of half-ester functional group and the effect was the same under the 29% ratio of half-ester functional group.
    a) The same property modifying effect of the additives has been demonstrated by the same extent of shifting in crossover frequencies measured by oscillatory rheometry, in FT-IR area ratios of characteristic vibration of functional groups and in elongation at break.
    b) Based on ratios of the integrated FT-IR areas belonging to the characteristic vibrations of olefin-maleic-anhydride copolymer based additives have been found to have an indirect antioxidant effect in waste HDPE presumably by hindering the degradation reactions.
2. Based on the results of isothermal test of waste HDPE/EVA blends with different composition it has been found that reactions taking place during processing can be estimated by monitoring changes in storage modulus as a function of time. Furthermore, changes in properties of the blends processed at different temperatures can be connected with the time-point belonging to the 5% change of the initial storage modulus and with the value of storage modulus measured in that time-point.
3. Relationships have been found among composition, mechanical, structural and rheological properties of the blends studying waste HDPE/EPDM 70/30 containing EPDM particles with six different fractions (0.00-0.25 mm; 0.25-0.40 mm; 0.40-0.63 mm; 0.63-1.00 mm; 1.00-1.25 mm and 0.00-1.25 mm).
    a) Linear viscoelastic range of the blends has been shown to be extended by addition of the whole fraction of EPDM particles (0.00-1.25 mm) compared to that of the fractions containing larger particles such as 0.40-0.63 mm; 0.63- 1.00 mm and 1.00-1.25 mm.
    b) Concept of ’apparent molecular weight’ has been introduced based on the data of crossover frequencies belonging to waste EPDM filler containing polymers, furthermore, the apparent molecular weight of different blends has been found to be estimated compared to each other based on the crossover frequencies.

c) Relationship between the crossover frequency and homogeneity from dispersion of the particles has been found to exist. The blend having the highest crossover frequency has been demonstrated to have the lowest apparent molecular weight parallelly with the best particle dispersion in the matrix material. Blend containing particles with the smallest particle size (0.00-0.25 mm) possessed the highest apparent molecular weight and showed the greatest tendency to agglomerate based on the apparent molecular weights and SEM micrographs.

d) It has been found that the crossover frequency of a blend can be estimated from the particle size distribution of a given waste elastomer fraction based on the crossover frequencies of the blends containing fractions of smaller particle domains measured by oscillatory rheology.

4. Effect of olefin-maleic-anhydride copolymer based additives has been examined at a maximum concentration of 0.2% in blends with different compositions.

a) The concept of 'apparent molecular weight' formulated in the sub-thesis 3./b) has been found not to be valid for the blends of 70/15/15 waste HDPE/GTR/EPDM because the crossover frequencies of those blends are influenced by the additive either besides the particle size and distribution of the waste elastomer.

b) Functional groups of the additives have been demonstrated not to be additive if two olefin-maleic-anhydride copolymer based additives are combined in the blend of 70/15/15 waste HDPE/GTR/EPDM since that did not result in summarized mechanical and melt rheological properties and molecular interactions prevailed by addition of the same additives separately in the same concentration presumably related to the postreactions of the additives.

c) It has been found that the similar half-ester ratio of the examined additives applied at the concentration of 0.1% caused similar crossover frequencies in the blends of 70/15/15 waste HDPE/GTR/EPDM. Increasing concentration of the same additives resulted in an inverse shift between crossover frequencies and values of elongation at break. Application of additives at 0.2% and with different contents of half-ester functional group caused the same crossover frequencies, therefore it has been demonstrated that no correlation between additive structures and the crossover frequencies and mechanical properties of the blends exists.

d) Mechanical properties of 70/30 waste HDPE/PEGTR20 blends have been found to decrease or remain unchanged compared to the additive-free blend if the additive did not possess half-ester content but the nitrogen containing functional groups were dominant. Significant increase of half-ester content (above 29%) in parallel with decrease the ratio of nitrogen containing functional groups resulted in the increment of elongation at break. Charpy impact strength has been demonstrated to improve with balanced ratio of the functional groups.

e) Based on location of the crossover frequencies effects originated from structural differences of the examined additives have been found not to prevail in 70/30 waste HDPE/PEGTR5 and 90/5/5 c-PP/GTR/EPDM blends.

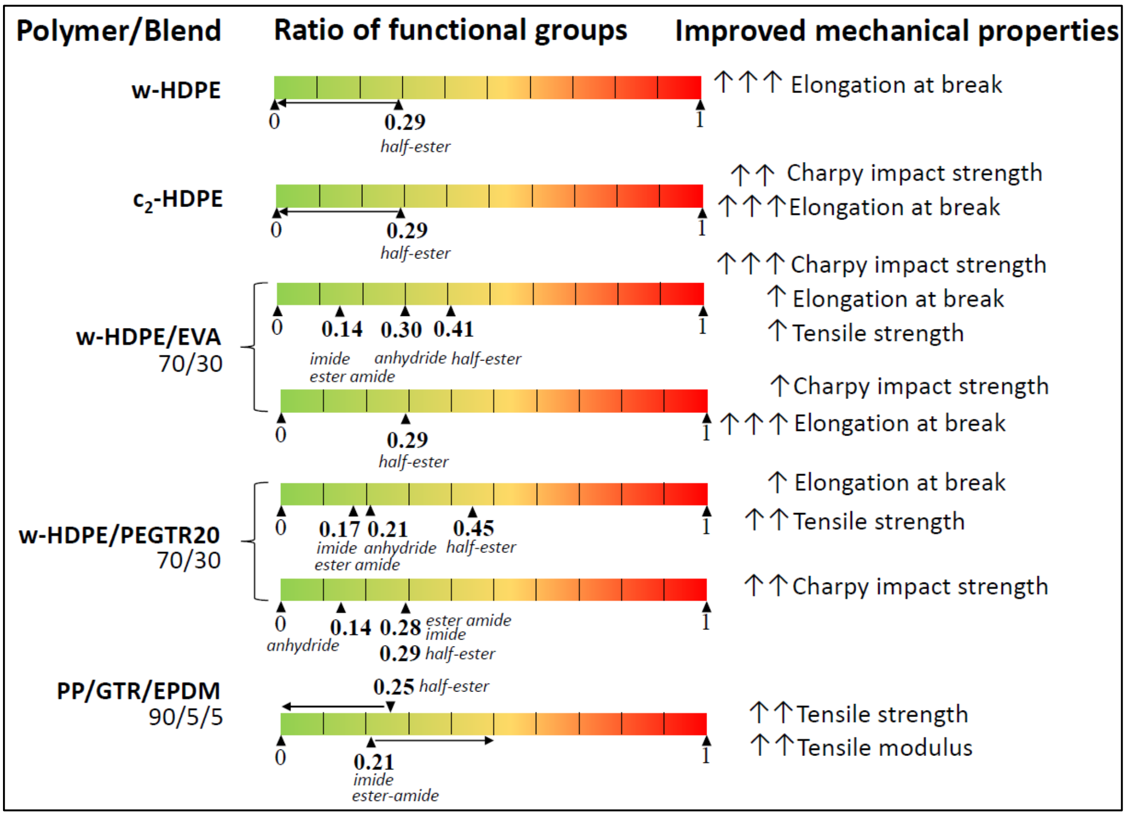
5. Practical applicability of research findings

As one of the results of the experimental work narrow range of unique recycling methods typical for waste based systems can be extended. *Mechanical properties can be planned more precisely and remain within a predictable range applying new knowledge about the effects of additive structure.*

Evaluation of the FT-IR spectra of the compatibilizing additive may be sufficient before incorporation of that into a neat polyolefin for improving mechanical properties since its expected effect can be estimated *making preliminary additive selection easier*.

Based on an oscillatory rheometry method on the one hand, *homogeneity related to the dispersion of waste elastomer particles can be detected numerically*. *Thereby, optimal range of the elastomers particle size can be determined before mixing* to achieve the best mechanical properties in the polymer. On the other hand, reactions taking place during the processing of HDPE/EVA blends can be estimated as a function of processing time and *the processing time may be optimized in that way*.

Effects of experimental additives having on mechanical properties of the examined material systems have been summarized the figure below supplemented by optimal ratio/range of the functional groups of the additives.



Experimental blends can be applied in any fields where there is no special requirement for purity and colour. Waste HDPE/waste elastomer based experimental blends can be used for example as a storage box, dog kennel cover, cat litter tray or a sport equipment (e.g. hockey puck), meanwhile experimental waste HDPE/EVA blends can serve as agricultural films.

6. Publications

Base journal papers of the PhD dissertation

Foreign journal papers

1. L. Simon-Stőger, Cs. Varga, E. Greczula, B. Nagy: A journey into recycling of waste elastomers via a novel type of compatibilizing additives, **Express Polymer Letters**, 13, 443-445, **2019**. (**Q1**; IF: 3,083 (2019))
2. L., Simon-Stőger, Cs. Varga: Valorization of waste polyethylene by blending with ethylene-vinylacetate and incorporating a new type of compatibilizer, **Journal of Vinyl and Additive Technology,** 1-15. https://doi.org/10.1002/ vnl.21806, **2020**. (**Q3**; IF: 1,550 (2019))
3. L., Simon-Stőger, Cs. Varga: PE-contaminated industrial waste ground tire rubber: how to transform a handicapped resource to a valuable one, **Waste Management**, 119, 111-121, **2021**. (**D1**; IF: 5,448 (2019))

Hungarian journal papers

1. Simon-Stőger, L. Heller, B. Greczula, E. Varga, Cs.: Hulladék gumiőrleményt tartalmazó blendek tulajdonságainak javítása, **Műanyag- és Gumiipari Évkönyv**, XV. évf. 72-80, **2017**. ISSN: 1589-6269
2. Simon-Stőger, L. Mudra, Á.K., Greczula, E. Varga, Cs.: Harmadik komponens hatása hulladék gumiőrleményt tartalmazó poliolefin kompozitokban, **Műanyag- és Gumiipari Évkönyv**, XVI. évf. 88-95, **2018**. ISSN: 1589-6269
3. Simon-Stőger, L., Hangyási, K., Kéri, K., Varga, Cs.: Olefin-maleinsav-anhidrid kopolimer alapú adalékok hatása polietilén blendekben, **Műanyag- és Gumiipari Évkönyv**, XVII. évf. 43-48, **2019**. ISSN: 1589-6269
4. Varga, Cs., Simon-Stőger, L., Martinecz, R., Katona, A.R.: Kísérleti kompatibilizáló adalékok tanulmányozása oszcillációs reometriával, **Műanyag- és Gumiipari Évkönyv**, **2021**. *megjelenés alatt*

Other journal papers

Foreign journal papers

1. B., Nagy, Cs., Varga, K., Kontos, L., Simon-Stőger: Remarkable role of experimental olefin-maleic-anhydride copolymer based compatibilizing additives in blends of waste PET bottles and polyamide, **Waste and Biomass Valorization**, https://doi.org/10.1007/s12649-020-01253-5, **2020**. (**Q2**; IF: 2,851 (2019))

Conference lectures

International conference lectures

1. L., Simon-Stőger, Cs., Varga: Effects of processing temperature on mechanical properties of waste high density polyethylene/ethylene viny acetate blends, **44th International Conference of Slovak Society of Chemical Engineering**, Demänovská Dolina, Liptovský Mikuláš, Szlovákia, **2017**. május 22-25. ISBN: 978-80-89597-58-1
2. L., Simon-Stőger, Cs., Varga: A possible way how to effectively combine waste elastomer fillers and waste polyethylene, **2nd International Conference on Energy, Environment and Climate Change**, Pointe Aux Piment, Mauritius, **2017**. július 5-7.
3. L., Simon-Stőger, Cs., Varga: Impact assessment of experimental olefin-maleic anhydride copolymer based additives in elastomer containing waste polyethylene, **Danube Vltava Sava Polymer Meeting,** Bécs, Ausztria, **2017**. szeptember 5-8. ISBN: 978-3-9504017-6-9
4. L., Simon-Stőger, Cs., Varga, L., Bartha, A., Kondor: A useful tool for creating connection between waste rubbers and polyolefins, **Baltic Conference Series**, Stockholm, Svédország, **2018**. május 14-17. ISBN: 978-91-88252-10-4
5. L., Bartha, Cs., Varga, L., Simon-Stőger: The effects of compatibilizer type additives in plastic and rubber composites, **Baltic Conference Series**, Stockholm, Svédország, **2018**. május 14-17. ISBN: 978-91-88252-10-4
6. L., Simon-Stőger, Cs., Varga, B., Nagy, K., Kéri: Novelty in recycling of waste elastomers in HDPE/PP blends by experimental compatibilizers, **22nd International Conference on Composite Materials**, Melbourne, Ausztrália, **2019**. augusztus 11-16.
7. B., Nagy, Cs., Varga, L., Simon-Stőger: Influence of novel types of olefin-maleic-anhydride copolymer based additives in blends of PA and recycled PET, **22nd International Conference on Composite Materials**, Melbourne, Ausztrália, **2019**. augusztus 11-16.
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9. K., Hangyási, Cs., Varga, R., Nagy, L., Simon-Stőger: A novel types of compound for surface treatment of carbon nanotubes for more effective application in polymers, **16th International Conference on Environmental Science and Technology**, Rodosz, Görögország, **2019**. szeptember 4-7. ISSN: 1106–5516

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1. Simon-Stőger L., Varga Cs.: Különböző hulladék elasztomer típusú őrlemények hatása hulladék polietilénben, **Pannon Tudományos Nap**, Nagykanizsa, **2016**. október 13.
2. Mudra Á. K., Simon-Stőger L., Varga Cs.: Szén nanocső hatása polietilén/gumi kompozitban: Erősítőanyag vagy töltőanyag?, **PhD hallgatók anyagtudományi napja XVI.**, Veszprém, **2016**. november. 28.
3. Simon-Stőger L., Varga Cs.: Elasztomerek hatása polietilénben, **PhD hallgatók anyagtudományi napja XVI.**, Veszprém, **2016**. november. 28.
4. Simon-Stőger L., Varga Cs.: Hulladék elasztomer-tartalom növelésének hatása hulladék polietilénben, **Műszaki Kémiai Napok**, Veszprém, **2017**. április 25-27.
5. Greczula E., Simon-Stőger L., Varga Cs.: Hulladék elasztomerek alkalmazhatósága polipropilénben, **Műszaki Kémiai Napok**, Veszprém, **2017**. április 25-27.
6. Simon-Stőger L. Varga Cs.: Hulladék polietilénben minőségjavítása etilén-vinil-acetát hozzáadásával, **XI. Országos Anyagtudományi Konferencia**, Balatonkenese, **2017**. október 15-17. ISBN: 978-615-5270-40-6
7. Simon-Stőger L., Kéri K., Varga Cs.: Hulladék elasztomer típusú őrlemény szemcseméretének hatása a mechanikai jellemzőkre polimer blendekben, **Műszaki Kémiai Napok**, Veszprém, **2019**. április 16-18.
8. Simon-Stőger L., Varga Cs.: Hulladék, mint lehetőség: PE szennyező tartalmú gumiabroncs őrlemények értéknövelése kísérleti olefin-maleinsav-anhidrid kopolimer alapú kompatibilizáló adalék felhasználásával, **PhD hallgatók anyagtudományi napja XIX.**, Veszprém, **2019**. december. 2.