

N ACETOXY PHT HALIMIDE NAPI AS NEW H ABSTRACTING AGENT AT HIGH TEMPERATURE

Khedekar Yogesh Vasantao

Department of Chemistry, CMJ University, Shillong, Meghalaya

ABSTRACT

Ricinoloxazoline maleinate (OXA) was grafted by melt free radical grafting onto polyolefins and elastomers to produce new compatibilizers for polymer blends. Effects of initial monomer and peroxide concentrations on the degree of grafting, on the amount of residual monomer, and on the side reactions were investigated. Reactive compatibilizers could be prepared with a suitable choice of processing conditions and initial concentrations. These oxazoline functionalized polyolefins and elastomers were found to act as effective compatibilizers in polymer blends. Blends of polyolefins and polyamide 6 were compatibilized with two novel types of compatibilizers: oxazoline functionalized polymers prepared by grafting and functionalized polyolefins prepared by copolymerization using metallocene catalysts. Comparison was made with commercial compatibilizers. Effects of the compatibilizers on blend morphology and thermal, tensile, and impact properties were studied. All of the functionalized polyolefins were effective compatibilizers in polyethylene/polyamide 6 blends. They were able to reduce the particle size and attach the particles more firmly to the matrix. The toughness was improved, though usually at the cost of stiffness. Only functionalized polyethylene's prepared with metallocene catalysts were able to improve the stiffness and strength along with toughness. In commercial polyolefin composites, fillers are usually coated with a fatty acid to make them organophilic. Replacement of fatty acid coatings with polymeric compatibilizers was studied in polyethylene/aluminum hydroxide (PE/ATH) and polyethylene/magnesium hydroxide (PE/MH) composites. The polymeric compatibilizers were oxazoline grafted polyethylene prepared by melt free radical grafting, hydroxyl and carboxylic acid functionalized polyethylene's prepared with metallocene catalysts, and commercial functionalized polyethylene's. Adhesion fracture changed to cohesion failure when the fatty acid coating was replaced through the addition of polymeric compatibilizers. Improvement in both stiffness and toughness was achieved, and improvements in flammability properties achieved with ATH or MH were preserved when polymeric compatibilizers were used as adhesion promoters.

INTRODUCTION

Blending of polymers is a powerful way to produce materials with a desirable combination of properties unavailable with a single polymer. New market applications can be covered with minimum development costs. Typical, desired properties are improved melt process ability, impact strength, rigidity, thermal stability, solvent resistance, barrier properties, and reduced flammability. Other objectives of blending are to dilute polymers through addition of low-cost commodity polymers and to recycle industrial or municipal plastics waste.¹ Polymer blends are classified as miscible or immiscible depending on the structures of the single polymer components. Only a few polymer pairs form a thermodynamically miscible polymer blend, which can be expected to possess properties close to the linear average of those of the two components. Properties tend to be worse for immiscible blends since the interface between the phases represents a weak point through which stress is poorly transmitted.

Properties of immiscible blends depend on the morphology, which means that properties can be tailored through control of the morphology.^{2,3} Polymer blends are usually prepared with intensive mixing in the melt, and thus the size of the dispersed particles is determined by the balance of two forces: deformation and coalescence.⁴⁻⁷ Repulsive interactions between the components result in high interfacial tension between the phases. Lower interaction energy is achieved by a reduction in the interfacial area, which is achieved through increased size of the dispersed particles. The particles are then stretched under shear and broken up into smaller particles. Parameters affecting the balance are viscosity ratio,⁸ composition,⁹ elasticity,¹⁰ shear stress,¹¹ and interfacial tension.¹² The morphology of immiscible blends can be altered by compatibilization. Block or graft copolymers with particular segments that are capable of interacting with the blend components are added. The copolymers are designed so as to locate at the interface of the blend components, a given block blending with a given phase so that the two components are essentially bound together. The principal effects of interfacial modification are to reduce the particle size and to narrow the particle size distribution. This reduction in particle size comes about through a decrease in interfacial tension and reduced coalescence.

REVIEW OF LITERATURE

This work was carried out at Helsinki University of Technology, Laboratory of Polymer Technology between 1996 and 2004. The research was started during the National Technology Agency (TEKES) project 'Compatibilization and post modification – key technologies for new plastic materials' and was then continued in targeted research projects. The financial support from TEKES is gratefully acknowledged. I would like to express my gratitude to Professor Jukka Seppälä for his guidance and interest in my work, and for the opportunity to work in his research group. Special thanks go to Markku Heino for introducing me to the interesting research area of polymer blends. I would like to thank Charlotta Nyström for getting acquainted to grafting and compatibilization together with me. Those times were truly instructive and fortunately I could share them with her. I would like to thank Kimmo Hakala for the cooperation in creating connection between the functionalized polyolefins and compatibilization. His knowledge and patience in studying the preparation of functionalized polyolefins made it possible to have those materials available. I would also like to thank Santeri Paavola for continuing the research of functionalized polyolefins, and his interest in using them in different applications. I would like to express my gratitude to Barbro Löfgren for her support and numerous scientific discussions over the years. Thanks are extended to my co-authors Pirjo Hietaoja, Tuulamari Helaja, Johanna Launne, and Maija Korhonen for their valuable contribution. The students and trainees who helped during this work are also sincerely thanked. All colleagues and personnel of the laboratory are thanked for pleasant working atmosphere and many enjoyable moments. In particular, Jorma Hakala is thanked for the enthusiastic followup of latest results in the field of polymer blends.

RESEARCH METHODOLOGY

Polymer blends and their compatibilization have been extensively studied over the last decade in the Laboratory of Polymer Technology at Helsinki University of Technology. After commercial compatibilizers had been extensively studied in blends of polyolefins with engineering plastics, attention was turned to the development of new compatibilizers by free

radical grafting. Another main area of research was the synthesis of functionalized polyolefins using metallocene catalysts. With these polyolefins containing polar groups available, a natural further step was to apply them as compatibilizers in polymer blends. The aim of the present work was thus to demonstrate the ability of the novel functionalized polyolefins to compatibilize polymer blends, and to compare them with commercial compatibilizers in certain polymer compositions.

The paper summarizes the research reported in the six appended publications. Melt free radical grafting of ricinloxazoline maleinate (OXA) onto polyolefins and elastomers was investigated first (I). Effects of initial monomer and peroxide concentrations on the degree of grafting, on the amount of residual monomer, and on side reactions such as β -scission and crosslinking were investigated. With a suitable choice of processing conditions and initial concentrations, oxazoline grafted polyethylene (PE-g-OXA), ethylene propylene copolymer (E/P-g-OXA), and styrene ethylene/butylene styrene copolymer (SEBS-g-OXA) could be prepared and further studied as compatibilizers for blends of polyolefins with polyamide 6 and polybutylene terephthalate (II). Blends of polyethylene and polyamide 6 were compatibilized with two novel types of compatibilizers: oxazoline grafted polymers (III) and copolymers prepared through polymerization of ethylene with monomers containing functional groups (IV). Comparison with commercial compatibilizers was made. Effects of the compatibilizers on the morphology, thermal, and mechanical properties (tensile and impact properties) were studied. Indications of reaction between the end groups of the polyamide and the functional groups of the compatibilizers were of interest. When analogous copolymers of propylene were available, the same compatibilization procedure was studied for blends of polypropylene with polyamide, and the results were compared with those for some commercial compatibilizers.

RESULTS & CONCLUSION

Free radical grafting in melt is a widely used method in the preparation of reactive graft copolymers. Advantages of melt extrusion are the continuous reactor and lack of solvents, but effective mixing is required.^{45,46} Here, novel compatibilizers were prepared by melt free radical grafting of ricinloxazoline maleinate (OXA) onto PE, E/P and SEBS. Long-chain oxazolines are reported to be less toxic than maleic anhydride and glycidyl methacrylate, and their boiling points are well above those of MAH and GMA.^{47,48} Earlier, ricinloxazoline maleinate has been melt free radical grafted onto PE,⁴⁹⁻⁵¹ PP,^{52,53} polycaprolactone,⁵⁴ and poly(organophosphazenes).⁵⁵ Oxazolines react fast with carboxyl and amino groups, which makes them suitable for use in polymer blends containing these end groups. Melt free radical grafting was performed in a corotating twin-screw midiextruder at various temperatures depending on the melting temperature of the polymer. Effects of the initial monomer and peroxide concentrations on the degree of grafting, on the amount of residual monomer, and on the type and amount of side reactions were studied. Novel oxazoline functionalized polyolefins and elastomers were prepared by melt free radical grafting and were shown to act as effective compatibilizers in polymer blends. Functionalized polyolefins prepared by copolymerization using metallocene catalysts were also shown to act as compatibilizers. The effects of these novel compatibilizers were compared with the effects of some commercial compatibilizers in blends of polyolefins and polyamide 6 and in polyethylene/metal hydroxide composites. The following conclusions can be drawn from the studies described in this summary and in publications I-VI: Compatibilizing

polypropylene/polyamide 6 blends is more complicated than compatibilizing polyethylene/polyamide 6 blends. Both commercial compatibilizers and the prepared oxazoline grafted polyolefins and elastomers improve toughness. However, only elastomer based compatibilizers improve the impact strength of cracked samples, and in that case the stiffness is reduced. Functionalized polyolefins prepared with metallocene catalysts interact with the polyamide phase, but reduction in particle size is not easily achieved.

REFERENCES

1. Utracki, L.A., *Commercial Polymer Blends*, Chapman & Hall, London, 1998, pp. 85-97.
2. Paul, D.R., Barlow, J.W., *Polymer blends (or alloys)*, *J. Macromol. Sci.-Rev. Macromol. Chem. C18* (1980) 109-168.
3. Paul, D.R., Bucknall, C.B., *Introduction*, in *Polymer Blends, Vol I: Formulation*, Paul, D.R., Bucknall, C.B. (eds.), John Wiley & Sons, New York, 2000, pp. 1-14.
4. Favis, B.D., *Factors influencing the morphology of immiscible polymer blends in melt processing*, in *Polymer Blends, Vol I: Formulation*, Paul, D.R., Bucknall, C.B. (eds.), John Wiley & Sons, New York, 2000, pp. 501-537.
5. Elmendorp, J.J., Van der Vegt, A.K., *A study on polymer blending microrheology: Part IV. The influence of coalescence on blend morphology origination*, *Polym. Eng. Sci.* **26** (1986) 1332-1338.
6. Fortelny, I., *Breakup and coalescence of dispersed droplets in compatibilized polymer blends*, *J. Macromol. Sci.-Phys.* **B39** (2000) 67-78.
7. Wu, S., *Formation of dispersed phase in incompatible polymer blends: interfacial and rheological effects*, *Polym. Eng. Sci.* **27** (1987) 335-343.
8. Jordhamo, G.M., Manson, J.A., Sperling, L.H., *Phase continuity and inversion in polymer blends and simultaneous interpenetrating networks*, *Polym. Eng. Sci.* **26** (1986) 517-524.
9. Favis, B.D., Willis, J.M., *Phase size/composition dependence in immiscible blends: experimental and theoretical considerations*, *J. Polym. Sci., Part B: Polym. Phys.* **28** (1990) 2259-2269.
10. Van Oene, H., *Modes of dispersion of viscoelastic fluids in flow*, *J. Colloid Inter. Sci.* **40** (1972) 448-467.
11. González-Núñez, R., De Kee, D., Favis, B.D., *The influence of coalescence on the morphology of the minor phase in melt-drawn polyamide-6/HDPE blends*, *Polymer* **37** (1996) 4689-4693.
12. Luciani, A., Champagne, M.F., Utracki, L.A., *Interfacial tension in polymer blends*, *Macromol. Symp.*, **126** (1997) 307-321.
13. Aiji, A., *Interphase and compatibilization by addition of a compatibilizer*, in *Polymer Blends Handbook, Vol 1*, Utracki, L.A. (ed.), Kluwer Academic Publishers, Dordrecht, 2002, pp. 295-338.
14. Aiji, A., Utracki, L.A., *Interphase and compatibilization of polymer blends*, *Polym. Eng. Sci.* **36** (1996) 1574-1585.
15. Beyer, G., *Chemical reactions in polymers – possibilities of reactive extrusion*, *Int. Polym. Sci. Tech.* **22** (1995) 39-46.