NOVEL FUNCTIONALIZED POLYOLEFINS AS COMPATIBILIZERS IN POLYOLEFIN/POLYAMIDE 6 BLENDS AND POLYETHYLENE/METAL HYDROXIDE COMPOSITES

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Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Chemical Technology for public examination and debate in Auditorium KE 2 (Komppa Auditorium) at Helsinki University of Technology (Espoo, Finland) on the 8th of April, 2005, at 12 noon.

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 polyethylenes 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 polyethylenes prepared with metallocene catalysts, and commercial functionalized polyethylenes. 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.

PREFACE

Espoo, February 2005

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CONTENTS

LIST OF PUBLICATIONS

This thesis is based on the following six publications (Appendices I-VI), which are, throughout the summary, referred to by their Roman numerals.

I   Anttila, U., Vocke, C., and Seppälä, J., Functionalization of polyolefins and elastomers with an oxazoline compound, *J. Appl. Polym. Sci.* **72**, 877-885 (1999).

II   Vocke, C., Anttila, U., Heino, M., Hietaoja, P., and Seppälä, J., Use of oxazoline functionalized polyolefins and elastomers as compatibilizers for thermoplastic blends, *J. Appl. Polym. Sci.* **70**, 1923-1930 (1998).

III   Vocke, C., Anttila, U., and Seppälä, J., Compatibilization of polyethylene/polyamide 6 blends with oxazoline functionalized polyethylene and styrene ethylene/butylene styrene copolymer (SEBS), *J. Appl. Polym. Sci.* **72**, 1443-1450 (1999).

IV   Anttila, U., Hakala, K., Helaja, T., Löfgren, B., and Seppälä, J., Compatibilization of polyethylene/polyamide 6 blends with functionalized polyethylenes prepared with metallocene catalyst, *J. Polym. Sci., Part A: Polym. Chem.* **37**, 3099-3108 (1999).

V   Hippi, U., Korhonen, M., Paavola, S., and Seppälä, J., Compatibilization of poly(propylene)/polyamide 6 blends with functionalized poly(propylene)s prepared with metallocene catalyst, *Macromol. Mater. Eng.* **289**, 714-721 (2004).

VI   Hippi, U., Mattila, J., Korhonen, M., and Seppälä, J., Compatibilization of polyethylene/aluminium hydroxide (PE/ATH) and polyethylene/magnesium hydroxide (PE/MH) composites with functionalized polyethylenes, *Polymer* **44**, 1193-1201 (2003).

The author's contribution to the appended publications:

Publications I and III: Charlotta Nyström (née Vocke) and Ulla Hippi (née Anttila) were jointly responsible for the research plan, experimental work, interpretation of the results, and preparation of the manuscript.

Publication II: Charlotta Nyström and Ulla Hippi carried out the experimental work and interpreted the results; they prepared the manuscript with the assistance of Markku Heino and Pirjo Hietaoja.

Publication IV: Ulla Hippi was responsible for the research plan and experimental work and, jointly with Kimmo Hakala, interpreted the results and prepared the manuscript. Polymerization and characterization of the copolymers and interpretation of these results were carried out by Kimmo Hakala.

Publications V and VI: Ulla Hippi participated in the preparation of the research plan, interpretation of the results, and the preparation of the manuscript. Rheological measurements and interpretation of these results were carried out by Maija Korhonen. Santeri Paavola carried out the polymerization and characterization of the copolymers and interpreted these results in Publication VI.

NOMENCLATURE

AA	acrylic acid
ATH	aluminum hydroxide
ATH(SA)	stearic acid coated aluminum hydroxide
BA	butyl acrylate
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
E/BA	ethylene/butyl acrylate copolymer
E/BA/MAH	maleic anhydride grafted ethylene/butyl acrylate copolymer
E/GMA	ethylene/glycidyl methacrylate copolymer
E/P	ethylene/propylene copolymer
E/P-g-OXA	oxazoline grafted ethylene/propylene copolymer
FTIR	Fourier transform infrared spectroscopy
GMA	glycidyl methacrylate
HRR	heat release rate
NMR	nuclear magnetic resonance spectroscopy
MAH	maleic anhydride
MFI	melt flow index
MH	magnesium hydroxide
MH(SA)	stearic acid coated magnesium hydroxide
OXA	ricinoloxazoline maleinate
OXA_i	initial oxazoline concentration
PA6	polyamide 6
PBT	polybutylene terephthalate
PE	polyethylene
PE-co-COOH	ethylene/10-undecenoic acid copolymer
PE-co-NHMe	ethylene/ N-methyl-10-undecenylamine copolymer
PE-co-OH	ethylene/10-undecen-1-ol copolymer
PE-g-AA	acrylic acid grafted polyethylene
PE-g-OXA	oxazoline grafted polyethylene
PP	polypropylene
PP-co-OH	propylene/10-undecen-1-ol copolymer
PP-g-MAH	maleic anhydride grafted polypropylene
PP-g-OXA	oxazoline grafted polypropylene
ROOR	peroxide
$ROOR_i$	initial peroxide concentration
SA	stearic acid
SEBS	styrene ethylene/butylene styrene copolymer
SEBS-g-OXA	oxazoline grafted styrene ethylene/butylene styrene copolymer
SEM	scanning electron microscopy

SYMBOLS

δ	tensile stress (Pa)
ε	elongation at break (%)
E	tensile modulus (Pa)
E'	storage modulus (Pa)
E''	loss modulus (Pa)
M_w	weight average molar mass (g/mol)
tan δ	damping factor, E''/E'
T	temperature (°C)

1 INTRODUCTION

1.1 General background

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 processability, 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.[2,4]

Copolymers may be added as discrete third components or generated *in situ* during processing via interfacial reaction of blend components. Diblock copolymers more effectively improve the compatibility of a blend than do triblock, multiblock, or graft copolymers. This is most probably due to the presence of just one linkage bond,

which necessarily is at the interface, allowing the rest of the chain to penetrate into and form entanglements in the homopolymer phases. Despite the greater efficiency of diblocks, they have seldom been used in commercial applications since they exist for only a small number of monomer pairs. Thus, for most blends, no suitable block copolymers are available.[13,14]

There is much more flexibility in the synthesis of *in situ* graft polymers, since many polymers can be used as polymer backbones and functional group pairs suitable for linking are widely available.[15,16] The functional groups may be the reactive chain ends, such as amino or carboxylic acid groups in polyamide, which occur naturally in condensation polymerization. For addition polymers, functional groups can be placed along the chain by copolymerization or by grafting, or at the chain end by special techniques. The functional groups must be carefully selected to ensure that adequate reaction can occur within the limited time frame of melt processing. In *in situ* grafting, the compatibilizer may be placed directly at the interface, where it is needed.[17,18]

1.2   Functionalized polyolefins

Polyolefins are produced in high and continuously increasing volume, already about 100×10^6 tonnes/a,[19] and a wide material grade variety is available. Polyolefins are used in a wide range of applications since they provide an excellent combination of mechanical and chemical properties as well as processability. Deficiencies, such as lack of reactive functional groups in the polyolefin structure, have nevertheless limited some of the end uses, particularly those in which adhesion, dyeability, paintability, printability, or compatibility with other functional polymers is paramount. The lack of functionality is due to the sensitivity of the conventional Ziegler-Natta catalysts towards heteroatoms present in the functional monomers.[20,21]

At least three technologies are available to produce functionalized polyolefins. Probably the most widely utilized is the copolymerization with free radical catalysts at high pressure to produce acrylate functionality in polyethylene.[22] Another technology is polyolefin copolymerization using metallocene catalysts, since these catalysts are able to tolerate sufficient amounts of certain comonomers. Special features are needed in the comonomer structure, for example, a spacer between the polymerizable vinylic double bond and the functional group, and protecting groups around the functional group to hinder its reaction with the catalyst.[23] A large number of polar monomers have been copolymerized using metallocene catalysts, the most interesting ones containing hydroxyl, carboxylic acid or amino functionality.[20,21,24-27]

The third technology to produce functionalized polyolefins is post-modification by melt free radical grafting. The most frequently used monomers are maleic anhydride,

vinyl silanes, and methacrylates such as glycidyl methacrylate or hydroxyethyl methacrylate. Peroxides, a practical and inexpensive source of free radicals, are usually used to initiate the grafting. Unfortunately, side reactions occur, including homopolymerization of the monomer, cross-linking in polyethylene and β-scission in polypropylene. These competing reactions can be controlled with a careful design of processing conditions.[28-30] Another post-modification procedure is to utilize terminal double bonds of polyolefins by ene-type addition of maleic anhydride,[31,32] epoxidation[31,33] or hydrosilylation.[34]

1.3   Polyolefins with fillers

Properties of polyolefins can be altered through the introduction of fillers. In general, fillers increase stiffness, provide abrasion resistance, and reduce shrinkage of molded parts. Disadvantages include deteriorated toughness and difficulties in processing. Since fillers are often hydrophilic, adhesion between the filler surface and the polyolefin matrix tends to be poor. Nevertheless, the achievement of certain properties such as color, conductivity, and flame retardancy usually requires the introduction of fillers, sometimes even in high concentration.[35]

The character of filler surfaces can be modified through the use of coatings, which reduce the interfacial tension at the boundary of the filler surface and polyolefin matrix. Typical coating agents for the fillers used with polyolefins are fatty acids, like stearic acid, and their salts, which can react with the hydroxyl groups on the filler surfaces.[36,37]

As an alternative to coatings, functionalized polyolefins have been added to polyolefin based composites to improve the adhesion between the filler particles and the matrix.[38-40] Reactive groups readily interact with the functional groups on the filler surface, while long hydrocarbon tails are anchored to the polymer matrix through physical entanglements and van der Waals interactions.[40,41] Durable linkages between the filler and the matrix may thereby be formed. In fracture processes, this may result in cohesive failure within the polyolefin in place of the adhesive failure taking place between the filler and the polymer.[42]

1.4   Scope of the study

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 thesis summarizes the research reported in the six appended publications (**I-VI**). Melt free radical grafting of ricinoloxazoline 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 6, and the results were compared with those for some commercial compatibilizers (**II**, **V**).

Finally, attention was turned to the compatibilization of polymer composites. Fillers, like aluminum hydroxide (ATH) and magnesium hydroxide (MH), which are mainly added to create flame retardancy, are usually coated to render them organophilic. In this study (**VI**), the coating agent was replaced with polymeric compatibilizers. Commercial compatibilizers, copolymers prepared with metallocene catalysts and oxazoline grafted polymers were tested. Effects of the compatibilizers on the morphology and the mechanical and thermal properties were investigated. Changes in the flammability properties were checked.

2   EXPERIMENTAL

2.1   Materials

A wide range of commercial polymer grades was used in the preparation of the blends. Polyethylene (PE), polypropylene (PP), polyamide 6 (PA6), and polybutylene terephthalate (PBT) were used as main components of the blends. PE, PP, ethylene/propylene copolymer (E/P), and styrene ethylene/butylene styrene copolymer (SEBS) were functionalized by melt free radical grafting. Commercial compatibilizers were either ethylene or propylene based and functionalized with butyl acrylate (BA), maleic anhydride (MAH), glycidyl methacrylate (GMA), or acrylic acid (AA). A summary of the commercial polymer grades is given in Table 1.

In the functionalization of polyolefins and elastomers by free radical grafting, a low volatile ricinoloxazoline maleinate (OXA, Loxamid V-EP 8515, supplied by Henkel KGaA) was used as monomer. The peroxide initiators were 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (Trigonox 29-C90), cumyl hydroperoxide (Trigonox K-95), and bis(*tert*-butylperoxyisopropyl)benzene (Perkadox 14S-fl), all supplied by Akzo.

Table 1.   Commercial polymers used in this work.

	Polymer	Grade	Supplier	Publication
PE/PA6 blend	PE	L 420 C	Borealis Polymers	II
	PE	LE 1804	Borealis Polymers	III, IV
	PA6	Ultramid B4F	BASF	II, III, IV
PP/PA6 blend	PP	VC12 33B	Borealis Polymers	II
	PP	HE125MO	Borealis Polymers	V
	PA6	Ultramid B3S	BASF	II, V
PP/PBT blend	PP	VB19 50K	Borealis Polymers	II
	PBT	Grilpet XE 3060	EMS Chemie	II
with fillers	PE	FA6220	Borealis Polymers	VI
in grafting	PE	LE7518	Borealis Polymers	I, II, III
	SEBS	Kraton G-1652	Shell	I, II, III
	E/P	Hifax CA10A	Montell	I, II
	PP	Valtec CL 101D	Montell	II
as commercial compatibilizers	E/BA/MAH	ME 0420	Borealis Polymers	V, VI
	PP-g-MAH	BB125E	Borealis Polymers	V
	E/BA	LE 6471	Borealis Polymers	VI
	E/GMA	Lotader AX 8840	Atofina	VI
	PE-g-AA	Polybond 1009	Uniroyal Chemicals	VI

Copolymers of ethylene and 10-undecen-1-ol, 10-undecenoic acid, or *N*-methyl-10-undecenylamine and copolymers of propylene and 10-undecen-1-ol were synthesized in our laboratory with metallocene catalysts according to procedures described in publications **IV** and **V**. The resulting copolymers varied in molar mass (11-244 kg/mol) and content of functionality (0.1-1.2 mol %, 0.5-8.1 wt %). Molar mass distribution was mostly narrow (1.7-3.4).

In the study aimed at improving adhesion in polyolefin composites, the fillers were aluminum trihydroxide (ATH) and magnesium dihydroxide (MH). The ATH grades were untreated (Apyral 60D) and stearic acid (SA) coated (Apyral 60E) from Nabaltec. The stearic acid content of 60E was 1.0 wt % and the average particle size for both grades was 0.7-1.5 μm. The MH grades were untreated (Hydrofy G-1.5) and stearic acid coated (Hydrofy GS-1.5) from Nuova Sima. The stearic acid content of GS-1.5 was 0.8 wt % and the average particle size for both grades was 1.8 μm.

2.2 Melt free radical grafting

The melt free radical grafting was carried out in a corotating twin-screw midiextruder (DSM, capacity 16 cm^3, screw length 150 mm) under nitrogen atmosphere. The midiextruder has a back-flow channel and was operated batch-wise with a screw speed of 65 rpm. Before melting, the monomer and peroxide were allowed to absorb in the matrix material, which was in powder form. The absorption procedure was carried out at room temperature for at least 15 minutes. The grafting time was five minutes, after which the material was taken out of the extruder and cooled.

2.3 Blending and processing

Before melt blending the materials were dried in a dehumidifying dryer under conditions recommended by the material suppliers. The blends were prepared in a corotating twin-screw midiextruder (DSM, capacity 16 cm^3, screw length 150 mm) under nitrogen atmosphere. The midiextruder was operated batch-wise with a screw speed of 65 rpm. After three minutes mixing, the blend was injection molded with a mini-injection molding machine (DSM) into specimens for tensile, impact, and dynamic mechanical tests.

2.4   Determination of grafting yield

The functionalized samples were purified by dissolving them in boiling decane (PE) or xylene (E/P, PP, SEBS) and then by precipitating them with acetone at room temperature. With this procedure the free OXA and its possible homopolymers were separated from the grafted polymer. The relative grafting yield was determined by Fourier transform infrared spectrometry (FTIR) (Nicolet Magna 750) from thin compression molded films of the purified samples. The peak at 1671 cm^{-1}, attributed to a complex mode involving C=N stretching and oxazoline ring bending, was treated as a characteristic peak of the grafted OXA. Another peak at 1737 cm^{-1}, resulting from the ester group in the OXA, was used to verify the results. For PE the peak at 1464 cm^{-1} representing the methylene groups was chosen as reference. Correspondingly, for E/P copolymer and PP the reference peak was at 2723 cm^{-1}, representing the skeleton of the PP chain, and for the SEBS copolymer it was at 1601 cm^{-1}, representing the styrene blocks of the copolymer.

^{1}HNMR analysis (Varian Gemini 2000, 300 MHz, BB) was used to calculate precise grafting yields and to produce a calibration curve for the FTIR results. The samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 at 125°C, and the resonance of the solvent at the chemical shift 5.91 ppm was used as an internal standard. The content of OXA was calculated from the signals in the 3.5-4.3 region resulting from the seven protons of the oxazoline ring and the methoxy group. The protons of the PE, PP, E/P copolymer and the ethylene/butylene blocks of the SEBS copolymer produced a strong peak at 0.8-1.8 ppm, which was used as the reference.

2.5   Characterization of blends and composites

Melt viscosities of the blend components were measured with a Göttfert Rheograph 2002 capillary rheometer at processing temperature 250 °C. A die with a length to diameter ratio of 30/1 was used. The measurements included Rabinowitch correction, but Bagley correction was not made.

Tensile and impact properties were measured from the conditioned specimens (three to five days at 23 °C and 50% relative humidity), except for samples containing polyamide 6, which were dried for 16 h at 80 °C before mechanical testing. Tensile properties of the blends were characterized with an Instron 4204 testing machine with a test speed of 2 mm/min and with specimen type 1BA according to the standard ISO 527-1993 (E). Charpy impact tests of unnotched and notched specimens with dimensions of 4 x 6 x 50 mm^3 were made with a Zwick 5102 pendulum-type testing machine according to ISO 179-1993 (E).

Morphology of the blends was characterized from cryogenically fractured samples with a scanning electron microscope (SEM) (JEOL JSM-840A, JSM-6335F or Zeiss DSM-962). The fracture surfaces were coated with a thin layer of gold, platinum, or chromium before examination.

Thermal properties were characterized by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The DSC measurements were carried out with a Mettler Toledo Star DSC821 under nitrogen. The rates of cooling and reheating were 10 °C/min and the temperature range was from 25 to 250 °C. The DMA measurements were performed with a PerkinElmer DMA-7. Experiments were carried out under nitrogen using the three-point-bending geometry at a heating rate of 4 °C/min. The temperature range was –100 to 170 °C for PP/PA6 blends and –120 to 100 °C for PE composites. The rectangular specimen dimensions were 18 x 4 x 1.5 mm^3.

Flammability properties of the composites were characterized with a cone calorimeter under heat flux of 35 kW/m^2 according to the standard ISO 5660:1993 (E).

A Molau test[43,44] was made to determine whether chemical reaction had taken place between the compatibilizer and polyamide. A 0.2-g sample of chopped blend was shaken with 10 mL of formic acid, and the mixture was left to stand for 24 hours. Formation of a white colloidal suspension was an indication of polyethylene macromolecules grafted with polyamide. For FTIR studies, the mixture was filtered, and the undissolved part was shaken twice with a portion of formic acid for several hours to remove the neat polyamide. Finally, the residue was washed with water and dried overnight at 60 °C. The amount of amide and other functional groups in the filtered sample was determined with a Nicolet Magna 750 FTIR from thin compression molded films. The peak at 720 cm^{-1} representing methylene groups was chosen as reference.

3   RESULTS AND DISCUSSION

3.1   Melt free radical grafting

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 ricinoloxazoline maleinate (OXA) onto PE, E/P and SEBS. The structure of OXA is presented in Figure 1. 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, ricinoloxazoline 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,[56-58] which makes them suitable for use in polymer blends containing these end groups.[51,59-61]

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.
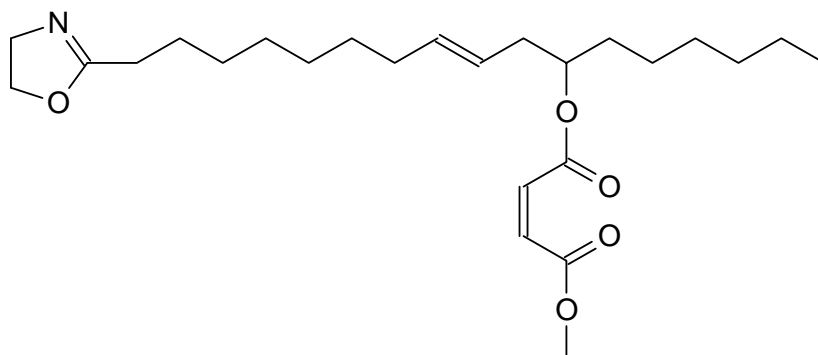

Figure 1. Chemical structure of ricinol oxazoline maleinate (OXA).

3.1.1 Effect of monomer and peroxide concentration

The initial monomer (OXA_i) and peroxide concentrations ($ROOR_i$) varied between 1.5 and 9.0 wt % and 0.15 and 0.90 wt %, respectively. The effect of the initial monomer concentration on the grafting yield and the residual amount of OXA is illustrated in Figure 2. The peroxide concentration was 6.7 wt % of the monomer concentration for PE and 10 wt % for E/P and SEBS. As expected, both the grafting yield and the residual amount of OXA increased with the initial monomer concentration. Grafting yields up to 2.1 wt % for PE, 2.3 wt % for E/P, and 2.7 wt % for SEBS were achieved.

Figure 3 shows the effect of the initial peroxide concentration on the grafting yield and the residual amount of OXA. The initial monomer concentration was 9.0 wt % for PE and 6.0 wt % for E/P and SEBS. The grafting yield increased with the initial peroxide concentration, and simultaneously the amount of residual OXA decreased. Thus, an increase in conversion and grafting efficiency was achieved with the peroxide addition. Conversions were at about 23% for PE and 30% for E/P and SEBS.

Figure 2. Effect of initial monomer concentration on the grafting yield (filled) and residual amount (open) of OXA for PE (■, □), E/P (▲, △), and SEBS (●, ○). T = 170 ^{o}C for PE, 200 ^{o}C for E/P, and 250 ^{o}C for SEBS. ROOR$_i$ / OXA$_i$ = 6.7 wt % for PE and 10 wt % for E/P and SEBS (**I**).
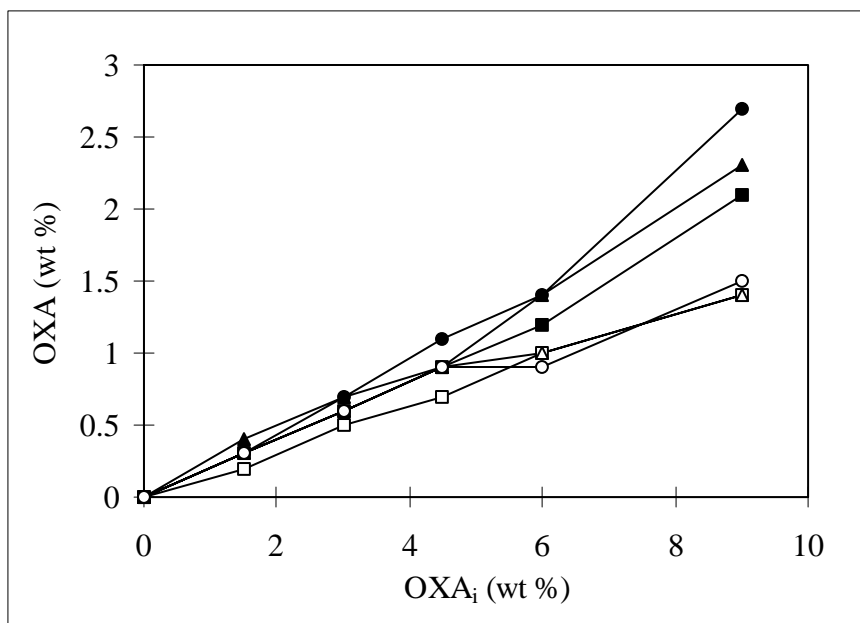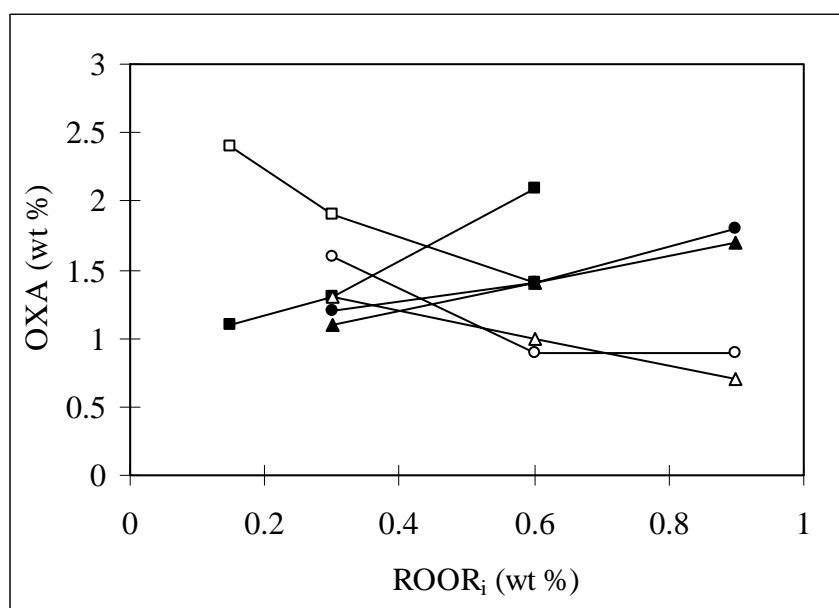

Figure 3. Effect of initial peroxide concentration on the grafting yield (filled) and residual amount (open) of OXA for PE (■, □), E/P (▲, △), and SEBS (●, ○). T=170 °C for PE, 200 °C for E/P, and 250 °C for SEBS. OXA$_i$ = 9.0 wt % for PE and 6.0 wt % for E/P and SEBS (data from **I**).

3.1.2   Controlling side reactions

Well-known side reactions in melt free radical grafting are crosslinking when polyethylene is grafted and β-scission when polypropylene is grafted. These reactions lead to inferior properties: the crosslinked polymer can no longer be melt processed and polymer with too low molar mass has poorer mechanical properties.[29,62] A scheme for the melt free radical grafting of OXA onto PE and PP and the side reactions is presented in Figure 4. PE contains mainly methylene groups, which after hydrogen abstraction form secondary macroradicals. These will react either with a monomer to form grafted polymer or with another macroradical to form crosslinked polymer. PP contains equal amounts of methyl, methylene, and methine groups. Because tertiary hydrogen atoms are three to four times as reactive as secondary hydrogen atoms at melt free radical grafting temperatures, the main macroradicals formed by hydrogen abstraction from PP are tertiary macroradicals.[28,29,63] Their competing reactions are grafting and disproportionation leading to β-scission.

In this study, changes in the polyolefin backbone were characterized by measuring the melt flow index (MFI), which gives some information about the processability of the polymer. A significant decrease in MFI was observed for PE, even with low monomer and peroxide additions, which indicated high extent of crosslinking. With suitable choice of peroxide and peroxide to monomer ratio, however, grafted PE could be produced with good grafting yield and without gel formation.

Since E/P and SEBS copolymers contain both secondary and tertiary hydrogen atoms in the polymer backbone, they can undergo either side reaction.[64,65] With low initial peroxide and monomer concentrations, the MFI increased as a result of β-scission. When the initial concentrations were increased, the MFI gradually decreased, probably because of the hydrogen abstraction of secondary hydrogen atoms and subsequent crosslinking. In grafting onto SEBS, crosslinking overcame β-scission with lower initial peroxide and monomer concentrations than in grafting onto E/P. This may have been due both to lower amount of tertiary hydrogen atoms in SEBS and to higher processing temperature, at which selectivity of hydrogen abstraction between methylene and methine decreases.
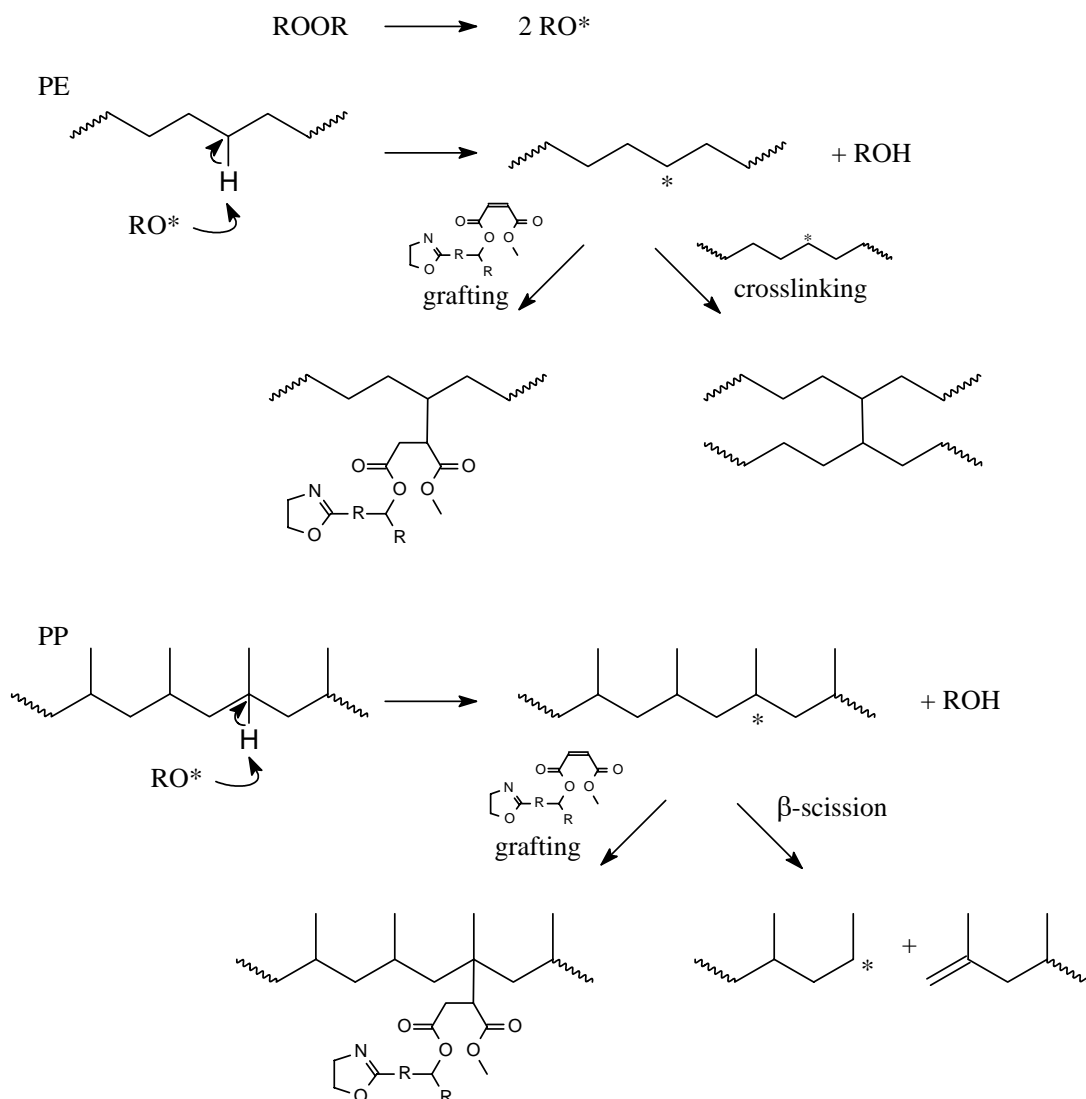
Figure 4. Scheme for the melt free radical grafting of OXA onto PE and PP and the side reactions, crosslinking and β-scission.

3.2 Oxazoline grafted polymers as compatibilizers

Graft copolymers are widely used as compatibilizers in blends of polyolefins with polyesters and polyamides. The most common compatibilizers are polyolefins grafted with monomers containing maleic anhydride or carboxylic acid groups.[1,66] These functionalities are able to react or form hydrogen bonds with the end groups of polyamides and polyesters.[67] Similarly, oxazoline group reacts with the amino and carboxylic acid end groups of polyamide, as shown in Figure 5.[57,68]
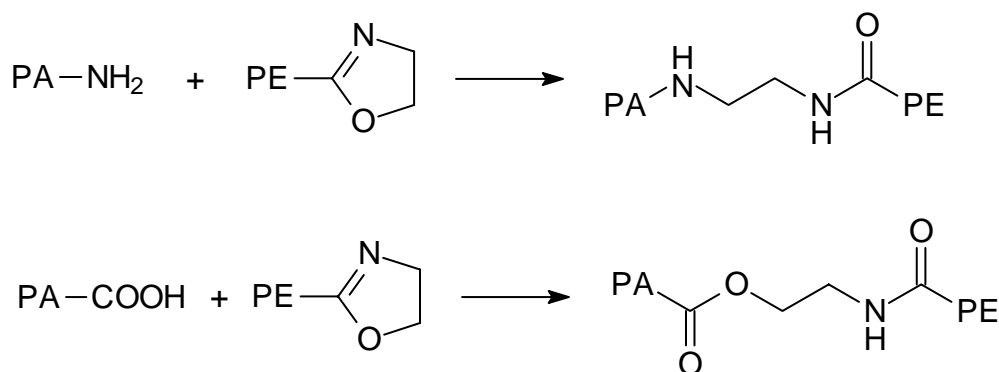
Figure 5. Reaction between polyamide 6 end groups and oxazoline grafted polyolefin.

With the oxazoline grafted polyethylene (PE-g-OXA), polypropylene (PP-g-OXA), ethylene/propylene copolymer (E/P-g-OXA), and styrene ethylene/butylene styrene copolymer (SEBS-g-OXA) in hand, it was of interest to test their capability as compatibilizers in blends of polyolefins with polyamides and polyesters in general. Polyamide 6 and polybutylene terephthalate were chosen as engineering plastics and their content was kept constant, 30 wt %, in all experiments.

For the PP/PA6 blends, PP-g-OXA, SEBS-g-OXA and E/P-g-OXA increased the Charpy impact strength of unnotched specimens and the elongation at break. The increase was less pronounced with PP-g-OXA, but together with improved tensile modulus and strength, a better balance among the tested properties was achieved.

For the PE/PA6 blends, compatibilization led to considerably improved Charpy impact strength of both unnotched and notched specimens, as shown in Figure 6. Tensile modulus and strength generally decreased when a compatibilizer was added.

Figure 6. Charpy impact strength for unnotched (bars) and notched (points) specimens of the PE/PA6 (70/30) blends with compatibilizer addition of 10 wt % (data from **II**).

For the PP/PBT blends, Charpy impact strength of unnotched specimens was again significantly improved by the compatibilization, and the impact strength of notched specimens increased with SEBS-g-OXA and E/P-g-OXA. As with PP/PA6 blends, only PP-g-OXA improved the toughness without sacrificing stiffness and strength.

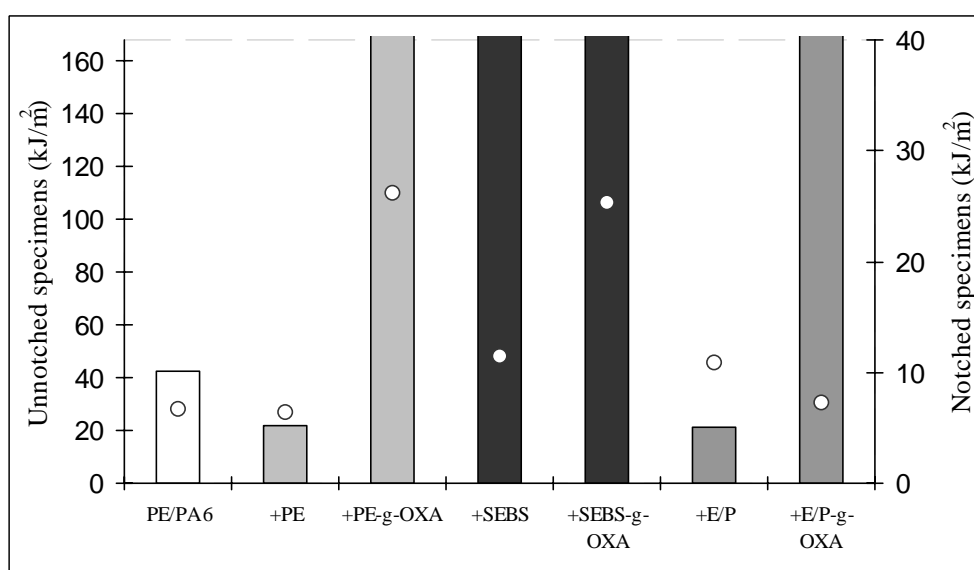Comparison of the ternary blends showed a marked difference in the compatibilizing effect between the functionalized compatibilizers and their unfunctionalized counterparts. When neat PE or PP was added to a blend, no noticeable difference appeared in the mechanical properties. Oxazoline functionalized PE or PP, on the other hand, caused a significant improvement in toughness; PE-g-OXA did this at the expense of stiffness and strength, but PP-g-OXA maintained these properties at the level of the binary blends. With unfunctionalized and functionalized SEBS or E/P, the stiffness and strength decreased because of the softness of these materials. The increase in toughness was more pronounced with the oxazoline functionalized polymers because of the reactions at the interface.

All uncompatibilized blends and all blends with unfunctionalized PE, PP or E/P showed coarse morphology. Neat SEBS slightly reduced the particle size. Addition of oxazoline grafted polymer resulted in much more uniform blend morphology; the particle size was generally reduced to less than 1.5 μm and the particles were much more firmly embedded in the matrix.

3.3   Compatibilization of PE/PA6 blends

Interest in blending polyethylene and polyamide is due to the differences in their properties, mainly the barrier properties. Polyethylene transmits oxygen and hydrocarbons but is resistant to moisture. Polyamide is highly sensitive to moisture but a good oxygen barrier. Thus, the main applications of the two polymers are in packaging films and containers requiring low permeability. Another unfortunate property of polyamides is their low resistance to stress in the presence of sharp notches or cracks, commonly evaluated as notched impact strength. To overcome this deficiency, polyamides have been blended with several types of impact modifiers, typically elastomeric or low modulus type olefinic polymers. Compatibilizers, which reduce the interfacial tension and stabilize the dispersed structure, can be added to improve the properties of polyethylene/polyamide blends.[69,70] In this study the compatibilization effect was evaluated for morphology and mechanical properties. As well, reactions between the compatibilizers and PA6 end groups were studied.

3.3.1 Compatibilization with oxazoline grafted polymers

The compatibilization effect of the oxazoline grafted PE and SEBS was further studied in the PE/PA6 blends with compositions covering the whole composition range. Comparison of the uncompatibilized blends showed the strength and stiffness to increase with the PA6 content. Toughness, on the other hand, was at lowest when the amounts of PE and PA6 were similar. As anticipated, addition of neat PE did not affect the mechanical properties. Because of its elasticity, neat SEBS slightly improved the toughness but at the cost of strength and stiffness. A significant improvement in toughness over the whole composition range was achieved with both functionalized compatibilizers, PE-g-OXA and SEBS-g-OXA. The elongation at break was more than five times as high with the blend composition of 20/80.

The uncompatibilized blends of all compositions tested showed visual evidence of the incompatibility between PE and PA6. In the PE/PA6 blends of compositions 80/20 and 60/40, where the PA6 formed the dispersed phase, the dispersion was in the form of rather large fibrils, which varied widely in size (1-8 and 1-20 μm, respectively). The size of the dispersed PA6 particles increased with the PA6 content, and at the composition 40/60 the structure of the blend appeared to be co-continuous. Since the PE/PA6 viscosity ratio was about 2, it was expected that the phase inversion region would lie at PA6 fraction more than 50 wt %. In the blend of composition 20/80, the size of the dispersed PE particles ranged from smaller than 1 μm to 3 μm. As could be predicted from the viscosity ratio, the dispersed PE particles were clearly smaller than were the dispersed PA6 particles in blends where PE formed the continuous phase.

With the addition of a compatibilizer, the particles of the dispersed phase became much more uniform and much reduced in size, as shown in Figure 7. The dispersed particles were smaller than 1 μm for all compatibilized blends and much more firmly embedded in the matrix. SEBS-g-OXA produced even smaller particles than did PE-g-OXA. The improved adhesion in the compatibilized PE/PA6 40/60 blends is seen as a rough interface instead of the smooth one in the uncompatibilized blend. The addition of neat SEBS reduced the particle size, but not as substantially as did the addition of its functionalized counterpart.

It is well known that the mechanical properties of a blend are dependent on the size distribution of the particles of the dispersed phase and on the adhesion between the separate phases. Thus, the binary blends having unstabilized morphology exhibited poor impact strength. Addition of a compatibilizer resulted in dispersed particles of uniform and very small size and the toughness was significantly increased. This was not the case when neat PE or SEBS was added to the blends, which indicates that, in the case of compatibilizer, a favorable reaction took place between the oxazoline group and the end groups of the PA6.
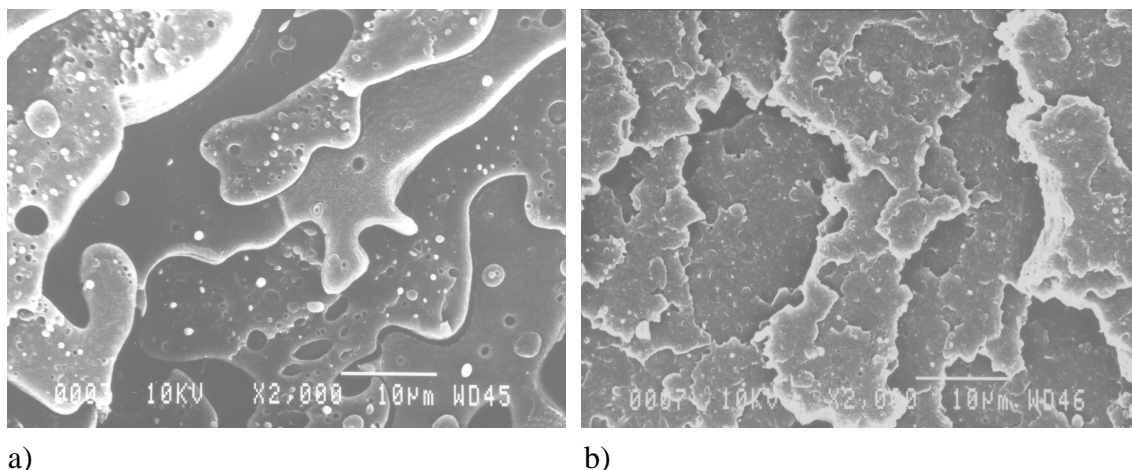
Figure 7. SEM micrographs (x2000) of a) uncompatibilized and b) SEBS-g-OXA compatibilized
PE/PA6 (40/60) blends (**III**).

3.3.2   Compatibilization with copolymers prepared with metallocene catalysts

Metallocene catalyst technology has offered a new route to functionalized polyolefins, and study was made of the effect of these copolymers as compatibilizers. The ethylene copolymers contained hydroxyl (PE-co-OH), carboxyl (PE-co-COOH), and *N*-methylamino functionalities (PE-co-NHMe). Since the oxazoline grafted polymers were found effective in compatibilizing PE/PA6 blends, the same blend, with composition 40/60, was selected for this study, too.

The primary aim of improving the toughness of the binary PE/PA6 blend was achieved with all functionalized copolymers. As shown in Figure 8, improvement was evident with an addition of 5 wt %, but with 10 wt % the increase in elongation at break and in Charpy impact strength of unnotched specimens was enormous. Surprisingly, addition of compatibilizer also increased the strength and stiffness. Again, the increase was dependent on the amount of compatibilizer added.

Figure 8. Charpy impact strength of unnotched specimens (bars) and elongation at break (points) of PE/PA6 blends with compatibilizer additions of 5 (gray) and 10 wt % (black). Compatibilizer is PE-co-OH with M_w of 123 kg/mol in B7 and B8, PE-co-OH with M_w of 136 kg/mol in B9 and B10, and PE-co-NHMe with M_w of 11 kg/mol in B14 and B15 (**IV**).

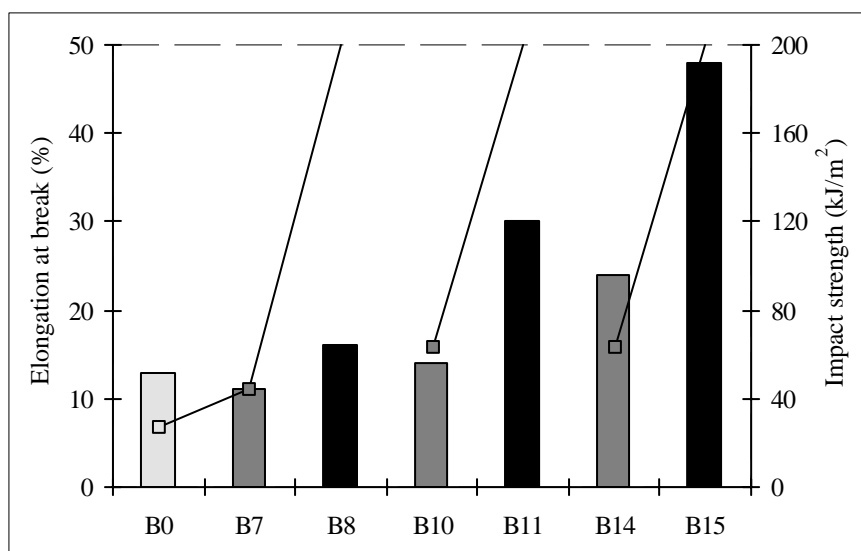Hydroxyl functionalized copolymers varied in their molar mass and content of functionality, and the greatest effect on the mechanical properties of the blends was found to be in line with the increasing molar mass of the compatibilizer. Stiffness improved with increasing molar mass from 44 to 136 kg/mol, while toughness improved slightly levelling off when molar mass was about 80 kg/mol. The content of the hydroxyl groups in the compatibilizers varied from 0.22 to 1.08 mol %. Since other properties changed at the same time, no relation was apparent between the increased functionality content in the compatibilizer and improved toughness in the corresponding blend. The copolymers with functionalities of carboxyl and secondary amino also proved to be effective as compatibilizers. In addition to toughness, there was substantial improvement in strength and stiffness, especially with the secondary amine. The same dependence between molar mass and Charpy impact strength as noted with hydroxyl groups was observed with carboxyl functionality.

Addition of all compatibilizers to the binary PE/PA6 (40/60) blend resulted in much finer morphology, as shown in Figure 9. Adhesion between the phases improved, evident as a ragged interface with much lower steps between the blend components. The addition of 5 wt % of compatibilizer also resulted in finer morphology, but did not disperse the smallest particles in the way the addition of 10 wt % did. No marked difference was observed between the compatibilizers with different functional groups.

a) PE/PA6/PE-co-OH   b) PE/PA6/PE-co-NHMe
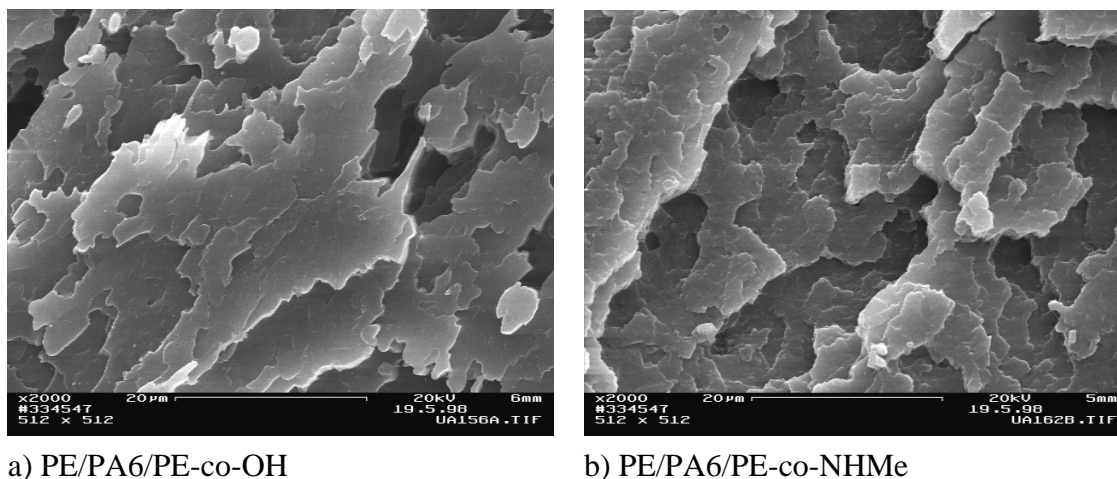
Figure 9. SEM micrographs (x 2000) of PE/PA6 (40/60) blends compatibilized with a) PE-co-OH and b) PE-co-NHMe (**IV**).

3.3.3   Compatibilization with commercial compatibilizers

Some commercial compatibilizers were tested to obtain a comprehensive overview of compatibilizer performance in the PE/PA6 (40/60) blend. Maleic anhydride grafted ethylene/butyl acrylate copolymer (E/BA/MAH) and ethylene/glycidyl methacrylate copolymer (E/GMA) were selected because these functionalities are capable of reacting with amino and carboxyl end groups of the PA6. Mechanical properties of PE/PA6 (40/60) blends compatibilized with these commercial compatibilizers are displayed in Table 2 along with representative results from the compatibilization studies with the new oxazoline grafted polymers and copolymers prepared with metallocene catalyst.

Comparison of the different compatibilizer showed the effectiveness of oxazoline grafted compatibilizers as toughness promoters. Functionalized copolymers prepared with metallocene catalyst improved stiffness as well as toughness. The commercial compatibilizer with maleic anhydride functionality improved toughness but at the cost of stiffness. E/GMA is a very soft material and its addition resulted in reduced stiffness and strength; surprisingly, no improvement in toughness was observed. Morphology studies showed that the PE/PA6 blend compatibilized with E/GMA was much rougher in structure than the other compatibilized blends (Figure 10).

Table 2. Tensile modulus (E), tensile stress (σ), elongation at break (ε), and Charpy impact strength of unnotched and notched specimens of PE/PA6 (40/60) blends with compatibilizer addition of 10 wt % (data partly from **III** and **IV**).

	E (MPa)		σ (MPa)		ε (%)		Charpy Impact Strength (kJ/m^2)			
							Unnotched		Notched	
PE/PA6 40/60	670	(7)	31.5	(1.2)	13	(3)	26.8 P	(8.0)	20.3 P	(8.6)
+ E/BA/MAH	529	(23)	34.5	(1.3)	43	(8)	NB		17.6	(3.3)
+ E/GMA	349	(25)	17.3	(1.2)	17	(1)	23.4	(12.7)	3.9	(0.6)
+ PE-g-OXA	612	(14)	30.9	(0.9)	51	(11)	NB		24.1 P	(10.8)
+ SEBS-g-OXA	547	(13)	27.7	(0.6)	83	(22)	NB		64.2 P	(24.0)
+ PE-co-OH	758	(31)	37.7	(1.8)	30	(16)	NB		31.7 P	(16.8)
+ PE-co-COOH	732	(18)	36.4	(1.2)	44	(11)	NB		12.1 P	(2.6)
+ PE-co-NHMe	765	(24)	42.1	(2.1)	48	(21)	NB		13.2 P	(3.9)

Standard deviation in parentheses, NB = nonbreak, P = partial break
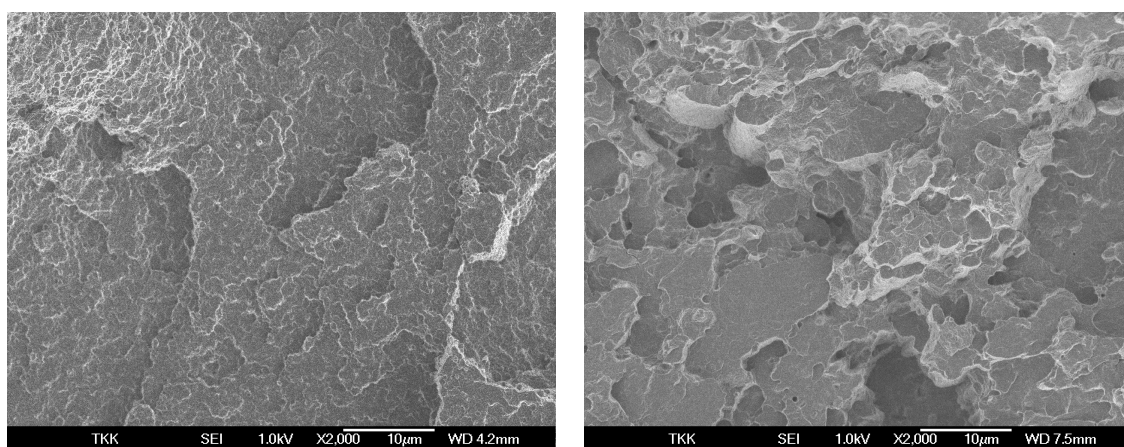
a) PE/PA6/(E/BA/MAH)   b) PE/PA6/(E/GMA)

Figure 10. SEM micrographs (x 2000) of PE/PA6 (40/60) blends compatibilized with a) E/BA/MAH and b) E/GMA.

3.3.4 Chemical reactions between blend components

Chemical reactions that were expected to take place between the compatibilizers and polyamide end groups were studied by the Molau test.[43,44] Mixing of polyethylene and polyamide in formic acid yields liquid formic acid with dissolved polyamide at the bottom and insoluble polyethylene on the top. Addition of a polymer component able to react with PA6 end groups and miscible with PE leads to the formation of a third phase, which appears as a white colloidal suspension in the liquid phase. The suspension is

formed of polyethylene particles surrounded by polyethylene macromolecules grafted with polyamide and, in this way, the insoluble polyethylene phase is also dispersed.

All the compatibilized blends formed a white colloidal suspension with formic acid, and, according to Molau[43] and Illing,[44] this can be considered as evidence of the reactions. To confirm this, the undissolved part was separated and characterized by FTIR. The IR spectra of some of the compatibilized blends are shown in Figure 11. Peaks due to the polyamide groups (1544, 1640 and 3300 cm^{-1}) were detected with all compatibilizers. In addition, a peak at 1734 cm^{-1} in the blends containing hydroxyl functionalized compatibilizers was an indication of ester groups formed through reactions between the hydroxyl groups in the compatibilizer and the carboxyl end groups in polyamide. Similarly, the reaction between the *N*-methylamino and carboxyl groups formed tertiary amide groups, which gave a peak at 1690 cm^{-1}. The blends containing carboxyl functionalized compatibilizers showed a peak at 1710 cm^{-1} derived from carboxylic groups that most probably formed hydrogen bonds with amido or amino groups of polyamide. Peaks giving information about covalent bonding between carboxylic functionality and amino end groups of polyamide unfortunately overlap with the strong peaks of amido groups in the PA6 backbone.
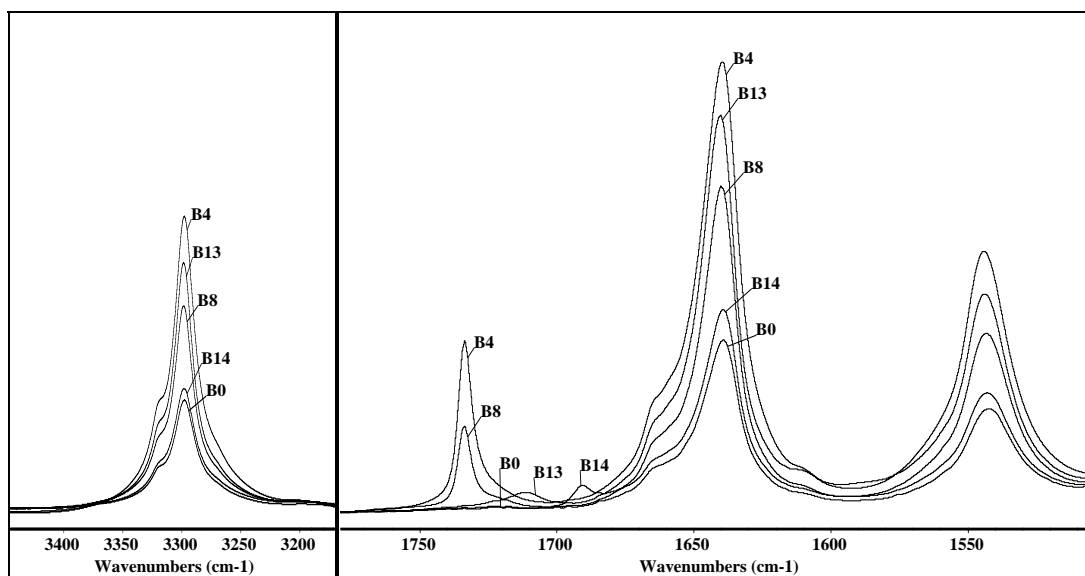

Figure 11. IR spectra of samples of PE/PA6 (40/60) blends with different compatibilizers obtained from the Molau test. Compatibilizer is PE-co-OH with hydroxyl content of 1.08 mol % in B4 and 0.56 mol % in B8, PE-co-COOH with carboxylic content of 0.46 mol% in B13 and PE-co-NHMe with amino content of 1.24 mol % in B14 (data from **IV**).

3.4   Compatibilization of PP/PA6 blends

The main incentives for developing polypropylene/polyamide blends have been the need to improve dimensional stability especially in humidity, to reduce water absorption, and to improve impact resistance of polyamide.[69-71] Again, achieving improvements in the properties requires compatibilization. PP/PA6 blend was first compatibilized in 1974. The compatibilizer was maleic anhydride grafted PP,[72] still one of the most effective and widely used compatibilizers in these blends.[66] Another effective procedure to compatibilize PP/PA6 blends is to add core-shell modifiers, which are maleic anhydride functionalized elastomers. The resulting morphology consists of a rigid PA6 core surrounded by a soft elastomeric shell in a polypropylene matrix. The reaction between the PA6 and the maleated elastomer, followed by the formation of an elastomeric interface at the PP/PA6 boundary, were responsible for enhanced particle dispersion and improvement in both toughness and stiffness.[73-76]

Compatibilizing of PP/PA6 (70/30) blends was studied with commercial compatibilizers, oxazoline grafted polymers, and hydroxyl functionalized copolymers prepared with metallocene catalysts. Mechanical properties of representative blends are displayed in Table 3. The primary aim, to improve toughness, was well achieved with oxazoline grafted polymers and to some extent with commercial maleic anhydride grafted compatibilizers. As expected, stiffness and strength of the blends were dependent on the properties of the matrix of the compatibilizers: when polypropylene based compatibilizers were used, the tensile modulus and strength increased, whereas with other compatibilizers it decreased. Copolymers prepared with metallocene catalysts were unable to increase Charpy impact strength, and elongation at break improved only with the copolymer with lowest hydroxyl content. Evidently very low hydroxyl contents may be sufficient for improving the adhesion. Another favorable feature of the compatibilizer with lowest functionality content was its ability to increase the stiffness and strength. On the other hand, the morphology studies showed that, despite the improved adhesion, the particles were still in ellipsoidal form, and this may have contributed to the high stiffness and strength. Other blends showed ellipsoidal structure, except the blends compatibilized with commercial PP-g-MAH and oxazoline grafted PP and SEBS. These blends showed more uniform particle size distribution with reduced particle size.

Table 3.   Tensile modulus (E), tensile strength (σ), elongation at break (ε), and Charpy impact strength of unnotched and notched specimens of PP/PA6 (70/30) blends (data from **II** and **V**).

	E (MPa)		σ (MPa)		ε (%)		Charpy Impact Strength (kJ/m^2)			
							Unnotched		Notched	
PP/PA6 70/30	877	(12)	37.9	(0.3)	16	(1)	15.2	(1.4)	2.2	(0.2)
+ E/BA/MAH	767	(44)	35.1	(0.3)	17	(2)	44.9	(8.7)	5.9	(0.6)
+ PP-g-MAH	900	(28)	38.7	(1.3)	16	(2)	26.5	(4.7)	2.0	(0.2)
+ PP-g-OXA	1018	(20)	39.3	(1.1)	50	(6)	37.4	(8.7)	2.2	(0.2)
+ SEBS-g-OXA	755	(41)	32.5	(0.9)	377	(99)	NB		3.6	(0.6)
+ E/P-g-OXA	738	(60)	34.8	(0.8)	331	(102)	NB		4.6	(0.4)
+ PP-co-OH1	929	(35)	38.6	(1.4)	54	(9)	12.6	(2.6)	1.7	(0.3)
+ PP-co-OH4	745	(17)	30.4	(1.0)	13	(1)			1.4	(0.1)

Standard deviation in parentheses, NB = nonbreak

Melting and crystallization behavior was studied for PP/PA6 blends compatibilized with commercial compatibilizers, copolymers prepared with metallocene catalysts, and oxazoline grafted polymers. In melting, the binary PP/PA6 blend exhibited two separate peaks originating from the melting of the PP and PA6 phases. This is typical for immiscible blends. Separate peaks of melting of the phases were seen for all compatibilizers, and there was no change in the melting behavior of the PA6 phase. Clear changes relative to the binary blend were observed only when the ethylene based compatibilizers were added: the melt enthalpy of the PP phase was somewhat lower and the peak was broadened, especially with E/BA/MAH.

The DSC crystallization thermograms of the uncompatibilized and various compatibilized blends are depicted in Figure 12. One crystallization peak for the polyolefin phase was observed for all blends, which is an indication of coincident crystallization of the compatibilizers and the matrix PP. The crystallization temperature of the PP matrix was 114.6 °C, while the corresponding temperature in the blend was 122.2 °C. This was expected since the solidified PA6 phase enhanced nucleation in the PP phase. With addition of PP-g-MAH as compatibilizer, the crystallization temperature of the PP phase was a further 5 °C higher. Since the particle size of the dispersed PA6 phase was then smaller there was more surface area available for nucleation at the interface. The hydroxyl functionalized propylene copolymers prepared with metallocene catalysts were unable to reduce the particle size of the dispersed PA6 phase, and the crystallization temperatures were close to that of the binary blend. The oxazoline grafted polypropylene did not change the crystallization temperature either, although it successfully decreased the particle size of the PA6 phase. When the ethylene based

compatibilizers E/BA/MAH, E/P-g-OXA, SEBS-g-OXA, and PE-co-OH were added to the blend, the crystallization temperature was lowered significantly. This behavior suggests kinetic hindrance of the nucleation effect of the PA6 particles, perhaps due to an additional interfacial layer prohibiting direct contact between the PP and PA6 phases.[77,78]
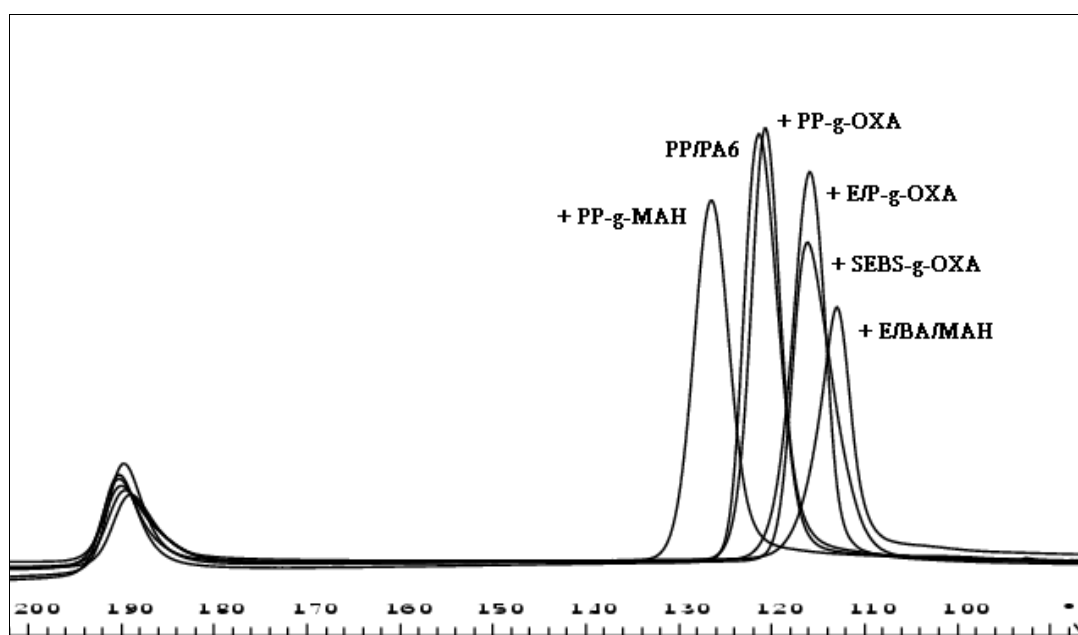

Figure 12. DSC cooling thermograms of uncompatibilized and some compatibilized PP/PA6 (70/30) blends with compatibilizer addition of 10 wt % (data partly from **V**).

3.5 Compatibilization of PE/ATH and PE/MH composites

Study was made of the ability of different polyethylene based compatibilizers to act as adhesion promoters in polyethylene composites. Aluminum hydroxide (ATH) and magnesium hydroxide (MH), with hydroxyl groups on their surfaces, are capable of interacting with functional groups and were selected as inorganic fillers for the study. These fillers are often coated with stearic acid to reduce interfacial tension between the filler particles and polyolefin matrix.[36] Polymeric compatibilizers were expected to form a more stable connection through reactions and entanglements with the components of the composites.

PE/ATH and PE/MH composites with composition 60/40 were compatibilized with functionalized polyethylenes: commercial polyethylenes containing butyl acrylate, maleic anhydride, glycidyl methacrylate, and acrylic acid functionalities; oxazoline grafted polyethylene; and hydroxyl and carboxylic acid functionalized ethylene copolymers prepared with metallocene catalyst. Mechanical properties of some of the

composites are presented in Figure 13. The addition of 40 wt % of ATH or MH caused a marked increase in the tensile modulus of polyethylene. Concurrently, however, the samples became much more brittle, as can be seen in the low values of Charpy impact strength and elongation at break. As expected, a moderate improvement in toughness was achieved with stearic acid coated fillers, but at the cost of stiffness and strength.
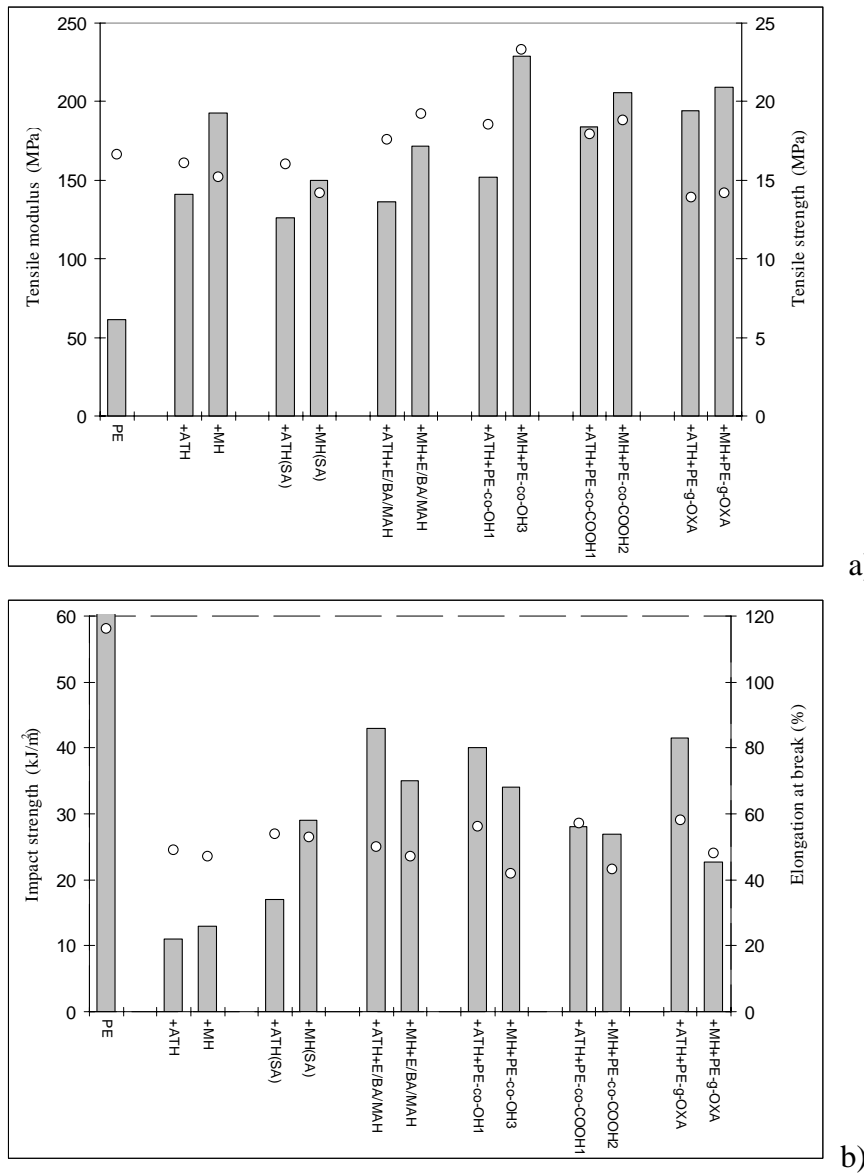

Figure 13. a) Tensile modulus (columns) and tensile strength (points) and b) Charpy impact strength of notched specimens (columns) and elongation at break (points), shown for PE/ATH and PE/MH (60/40) composites with compatibilizer addition of 10 wt % (data partly from **VI**).

When stearic acid treatment was replaced by an addition of functionalized polyethylene in the blending step, marked improvement was achieved in both stiffness and toughness. The result was the same with all three types of compatibilizers. Thus, the longer organic chain was shown to be beneficial to the mechanical properties of the composites.

Dynamic mechanical analysis was carried out on neat polyethylene and its composites to obtain further information on mechanical properties and molecular motions. The filler effect, an increase in storage modulus (E'), was clearly observed when ATH or MH was added to polyethylene. The increase in E' values was less when fillers were coated with stearic acid and greater when, instead, functionalized polyethylene was added as compatibilizer. The order of the curves at room temperature correlated with the order of the values of the tensile modulus. Tan δ curves showed a reduction in magnitude of the peak intensity and broadening of the peak for the β-relaxation upon addition of functionalized polyethylene. These are indications of restricted molecular motions, probably because the fillers are better attached to the matrix.[79,80]

Morphologies of the uncompatibilized and some compatibilized composites of PE with ATH and MH are shown in Figures 14 and 15. In composites without compatibilization (Figures 14a and 15a) particles clearly were not attached to the matrix. Similarly, when the particles were coated with stearic acid, debonding occured between the particles and the matrix (Figures 14b and 15b). An addition of 10 wt % of any of the polymeric compatibilizers improved the adhesion so much that the fracture mechanism changed from adhesion failure to cohesion failure. Evidently the particles were coated yielding smooth fracture surfaces in the composites. Even the larger MH particles were then better embedded in the matrix, and during fracture the filler particles split instead of pulling out of the matrix.

a) PE/ATH

b) PE/ATH(SA)
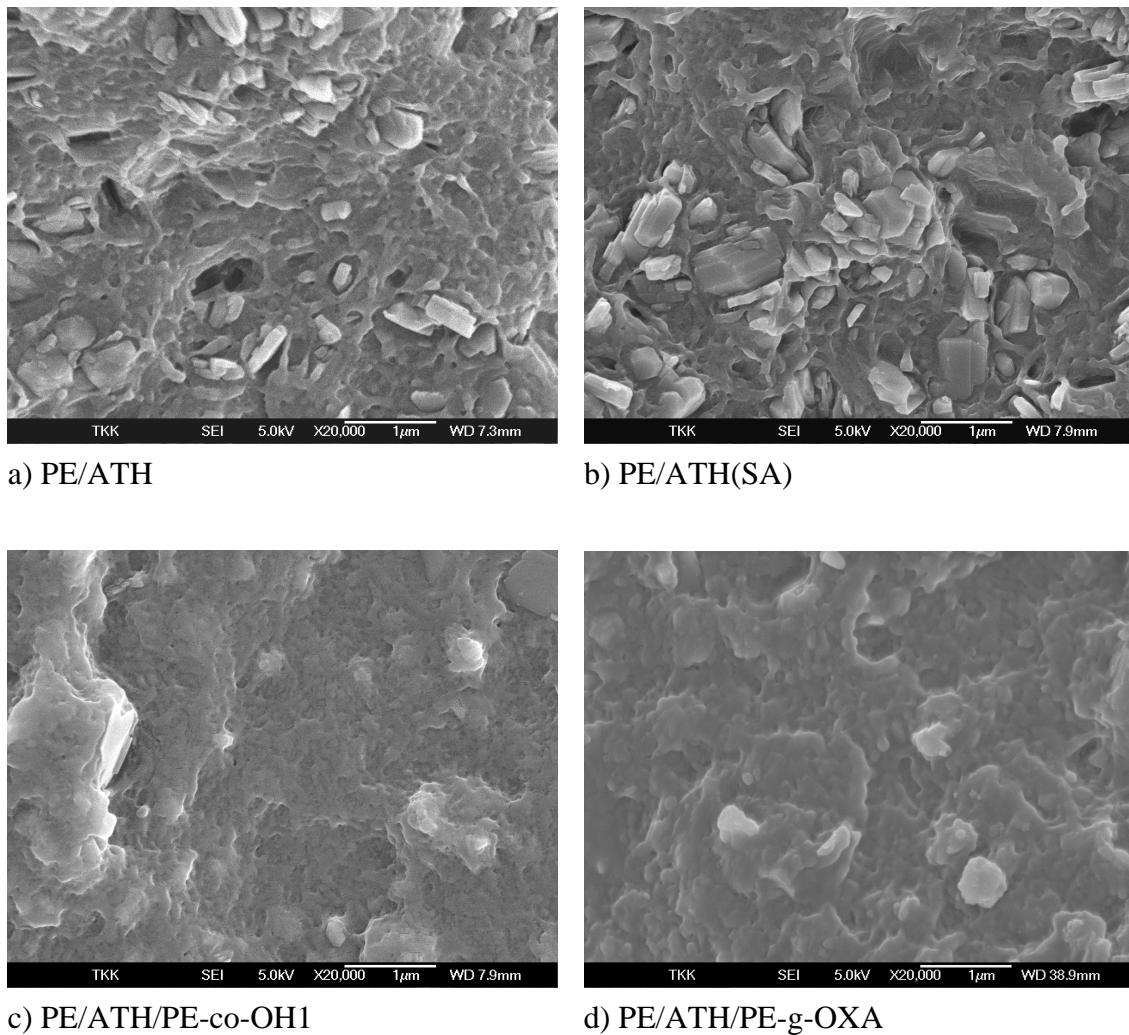
c) PE/ATH/PE-co-OH1

d) PE/ATH/PE-g-OXA

Figure 14. SEM micrographs of PE/ATH (60/40) composites (x 20 000). a) PE/ATH, b) PE/ATH(SA), c) PE/ATH/PE-co-OH1, and d) PE/ATH/PE-g-OXA (data partly from **VI**).

DSC measurements were carried out to evaluate the influence of ATH and MH particles on the melting and crystallization behavior of polyethylene, and to discover how the addition of functionalized polyethylenes further changed this. An addition of 40 wt % of ATH or MH to the polyethylene increased the crystallization temperature by about 3 °C, and the onset temperature even more. Thus, as expected, nucleation of the composites seems to be induced by the filler particles. Addition of polymeric compatibilizers lowered the intensity of the peak of the matrix polyethylene and broadened the area of crystallization, indicating some degree of co-crystallization.

a) PE/MH   b) PE/MH(SA)
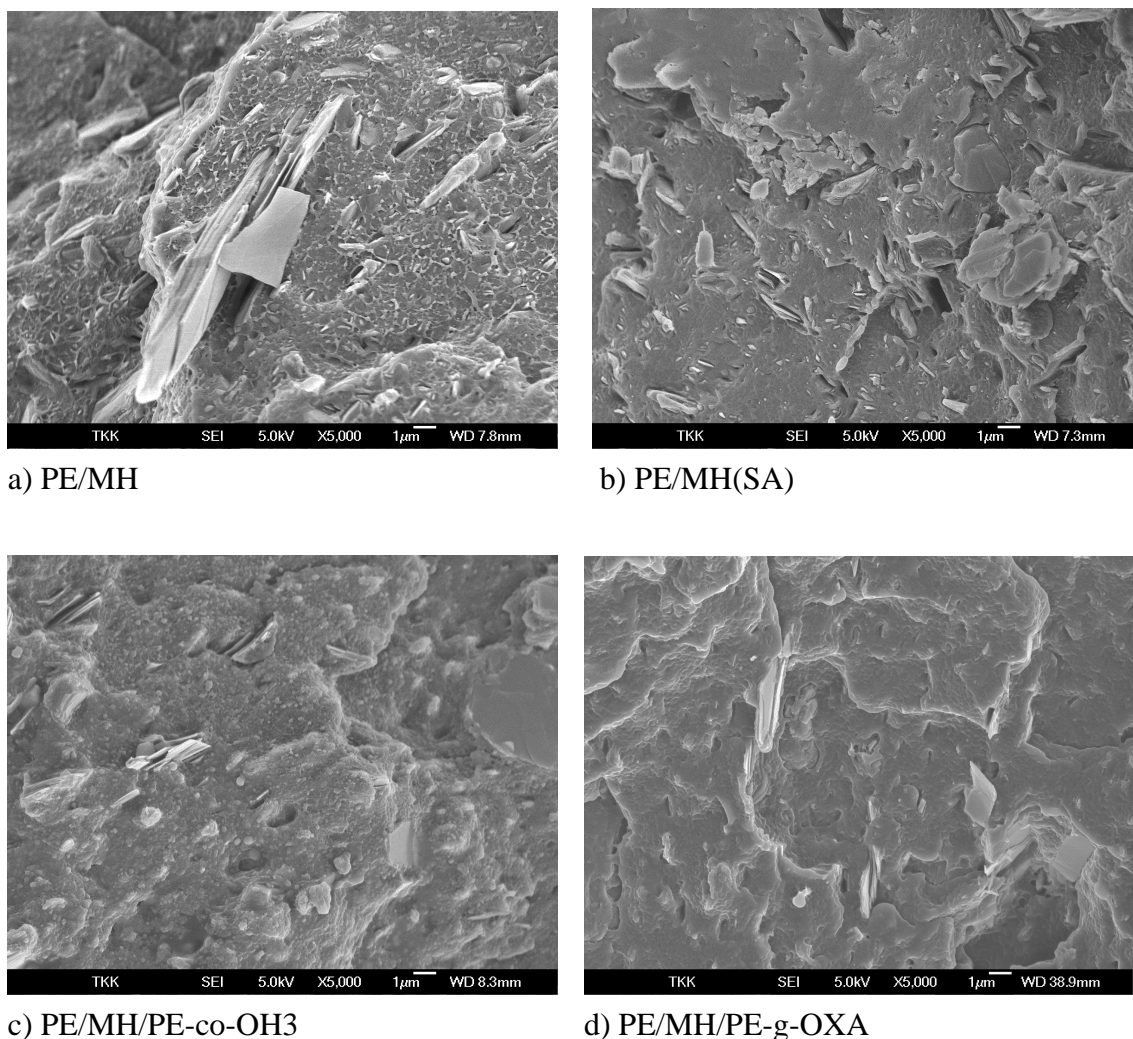
c) PE/MH/PE-co-OH3   d) PE/MH/PE-g-OXA

Figure 15. SEM micrographs of PE/MH (60/40) composites (x 5 000). a) PE/MH, b) PE/MH(SA), c) PE/MH/PE-co-OH3, and d) PE/MH/PE-g-OXA (data partly from **VI**).

Since ATH and MH are widely used flame retardants, measurements with a cone calorimeter were made to check for changes in flammability properties. Trends with ATH and MH composites were found to be similar. Times to ignition and heat release rate (HRR) for neat polyethylene and its composites with MH are shown in Figure 16. Neat polyethylene was ignited in 57 s and the HRR was as high as 1200 kW/m^2 at maximum. The addition of 40 wt % of untreated MH decreased the total heat released by 35%; the HRR was considerably lower and the time to ignition was 78 s, though the release lasted longer. Time to ignition of the composites with polymeric compatibilizers varied from 73 to 85 s and HRR from 438 to 573 kW/m^2. Rates of smoke and carbon monoxide production were also measured, and trends in the curves were very similar to those in the HRR curves. Thus, it was confirmed that the flammability properties of the composites are not negatively affected by the addition of polymeric compatibilizers.
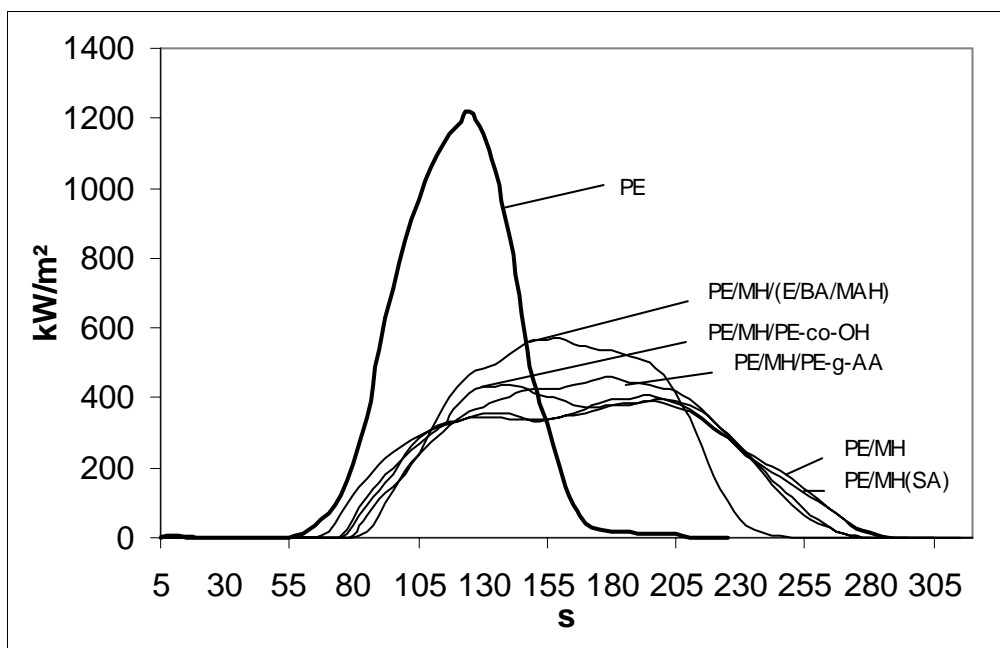
Figure 16. Heat release rate of neat polyethylene and its composites with MH (**VI**).

4   CONCLUSIONS

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**:

- Novel oxazoline functionalized compatibilizers can be prepared by free radical grafting in melt. Attention must be paid to temperature and initial monomer and peroxide concentrations to control the side reactions occurring along with the grafting. Under suitable conditions, reactive compatibilizers for polymer blends and composites can be produced.

- All three kinds of functionalized polyolefins used in this study are effective compatibilizers for polyethylene/polyamide 6 blends. They reduce particle size and better attach the particles to the matrix. Toughness is improved with all compatibilizer types studied, though usually at the cost of stiffness. Only functionalized polyolefins prepared with metallocene catalysts improve the stiffness and strength along with toughness.

- 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.

- Replacing a fatty acid coating of inorganic fillers with polymeric compatibilizer has many advantages. The adhesion failure typical of present coated products is changed to cohesion fracture with the addition of polymeric compatibilizers. This results in improvement in both stiffness and toughness. Improvements in flammability properties achieved with ATH or MH are preserved when polymeric compatibilizers are added as adhesion promoters.

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