ELSEVIER

Polymer 44 (2003) 1193–1201

polymer

www.elsevier.com/locate/polymer

Compatibilization of polyethylene/aluminum hydroxide (PE/ATH) and polyethylene/magnesium hydroxide (PE/MH) composites with functionalized polyethylenes

U. Hippi, J. Mattila, M. Korhonen, J. Seppälä*

Helsinki University of Technology, Laboratory of Polymer Technology, P.O. Box 6100, 02015 Hut, Finland

Abstract

Study was made of the compatibilization of polyethylene/aluminum hydroxide (PE/ATH) and polyethylene/magnesium hydroxide (PE/MH) composites with composition 60/40 wt%. Compatibilizers were hydroxyl or carboxylic acid functionalized copolymers prepared in our laboratory with metallocene catalysts and commercial butyl acrylate, maleic anhydride, epoxy, and acrylic acid functionalized polyethylenes. Comparison was made with stearic acid treatment of the composites. The effect of polymeric compatibilizers on the properties of the composites was studied by tensile and impact tests, dynamic mechanical analysis, differential scanning calorimetry, morphology studies, and flammability tests. Adhesion of the PE/ATH and PE/MH composites was significantly improved, as seen in morphology studies in the changed fracture mechanism. The improved adhesion was particularly reflected in the mechanical properties: an improvement in both stiffness and toughness was achieved with use of the functionalized copolymers prepared with metallocene catalysts. According to cone calorimetry, flame retardancy properties of the composites did not deteriorate upon addition of compatibilizers.

Keywords: Flame retardants; Compatibilization; Functionalized polyethylene

1. Introduction

Properties of polymers often can be altered through the introduction of fillers. In general, fillers increase stiffness, provide abrasion resistance, and reduce shrinkage of molded parts. Disadvantages may include deteriorated toughness and difficulties in processing. In particular, polyolefins, which are nonpolar, are incompatible with the common hydrophilic fillers. Thus, adhesion between the filler surface and the matrix is poor. The achievements of properties such as color, conductivity, and flame retardancy nevertheless usually requires the introduction of fillers, sometimes even in high concentration. For instance, to achieve the required flame retardancy, loadings of about 60 wt% of aluminum hydroxide (ATH) or magnesium hydroxide (MH) are needed. The character of the filler surface can be modified through use of different coatings, and thereby the degree of interfacial adhesion at the boundary between the filler and polymer matrix improves. Typical coating agents for fillers containing hydroxyl groups are fatty acids, like stearic acid, and their salts, which can react with hydroxyl groups. Advantage is improved filler dispersion, which enhances both mechanical properties, and lubrication, and lower melt viscosity [1–4].

In addition to coatings, polymeric compatibilizers have been added to polyolefin-based composites to improve the adhesion between filler particles and matrix [5]. The hydrophobic polyolefins are usually made more hydrophilic by copolymerization or grafting with polar monomers. Reactive groups interact readily with functional groups on the inorganic filler, and long hydrocarbon tails are able to anchor to the polymer matrix through physical entanglements and van der Waals interactions [6,7]. A durable connection between the filler and the matrix is thereby established. Short chains such as in stearic acid, are too short to entangle, but perfectly capable of reducing interfacial tension [6].

Polymeric compatibilizers that have been studied include acrylic acid functionalized polypropylene (PP-*g*-AA) [8–10], maleic anhydride functionalized polyethylene (PE-*g*-MAH) [5], polypropylene (PP-*g*-MAH) [6,11], and ethylene–propylene rubber (EPR-*g*-MAH) [12]. Also poly(*n*-butyl acrylate) (PnBuA) has been used as an additive for PE/MH composites [12]. Mai et al. [8] have studied PP/ATH composites containing different levels of ATH

---

* Corresponding author. Fax: +358-9451-2622.
E-mail address: jukka.seppala@hut.fi (J. Seppälä).

0032-3861/03/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(02)00856-X

modified by PP-*g*-AA. They noticed that the addition of PP-*g*-AA increased the strength and modulus, but the impact strength was lower than that of the unmodified composites. Hornsby and Watson [9] obtained improvement in flexural modulus and strength in PP/MH composites by adding PP-*g*-AA. Also impact strength was slightly improved. Similar results have been reported by Chiang and Hu [10], who noticed that addition PP-*g*-AA improved the tensile strength and impact resistance of PP/MH composites. However, elongation decreased with PP-*g*-AA addition.

In their study of polymeric coupling agents as property enhancers in highly filled polymer systems, Hausmann and Flaris [5] found that MAH-grafted polymers based on PP or PE are effective coupling agents between polymers and a variety of inorganic fillers, providing significant property enhancement. In PE/ATH blends the elongation at break increased with PE-*g*-MAH level.

Adhesion between ethylene copolymers and hydrated aluminum foil containing Al–OH groups has been studied by Strålin and Hjertberg [13] Copolymers were ethyl butyl acrylate (E/BA), ethyl vinyltrimethoxysilane (E/VS) and copolymers with both comonomers (E/VS/BA). All showed improved adhesion relative to PE alone. Adhesion between E/BA and Al–OH was assumed to be due to Lewis acid–base interactions.

We studied the usefulness of functionalized polymers as compatibilizers for PE/ATH and PE/MH blends, with the aim of improving mechanical properties of the blends through enhanced adhesion between filler and matrix. Commercially available functionalized polymers and hydroxyl or carboxylic acid functionalized ethylene copolymers prepared in our laboratory with metallocene catalysts were tested.

2. Experimental

2.1. Materials

The polyethylene used as matrix in ATH and MH blends was FA 6220 supplied by Borealis Polymers. It has a melt flow rate of 2.1 g/10 min (2.16 kg, 190 °C) and density of 922 kg/m^3. The ATH grades were untreated Apyral® 60D and stearic acid coated Apyral® 60E from Nabaltec. The stearic acid content of 60E was 1.0 wt% and the average particle size for both 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 was 1.8 μm. The commercial compatibilizers are described in Table 1.

Copolymers of ethylene and 10-undecenol or 10-undecenoic acid were prepared in our laboratory with commercial metallocene catalysts according to reported procedures [14–16]. The polymerization conditions and properties of the copolymers are given in Table 2. PE-*co*-OH1 and PE-*co*-COOH1 were used in ATH blends and PE-*co*-OH2-4 and PE-*co*-COOH2 in MH blends.

2.2. Blending and injection molding

The composites consisted of 60 wt% polyethylene and 40 wt% ATH or MH. The amount of compatibilizer (2, 5, or 10 wt%) was subtracted from the polyethylene phase. The commercial compatibilizers were dried overnight at 60 °C before blending. The blends were prepared in a corotating twin-screw midiextruder (DSM, capacity 16 cm^3, screw length 150 mm) with a screw speed of 65 rpm. The extrusion temperature was 170 °C for ATH blends and 180 °C for MH blends. After 3 min mixing, the blend was injection molded into tensile and impact test specimens with a mini-injection molding machine (DSM). The processing temperature was 180 °C for ATH blends and 200–220 °C for MH blends. With ATH blends the mold temperature was 80–100 °C for tensile test specimens and 50 °C for impact test specimens. Corresponding temperatures with MH blends were 45–75 and 45 °C. The higher values were needed with the polymeric compatibilizers prepared with metallocene catalysts.

2.3. Characterization of blends

Before testing of mechanical properties the injection molded samples were conditioned at 23 °C and 50% relative humidity for 3–5 days. Tensile properties were characterized with an Instron 4204 universal 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 the notched specimens with dimensions $4 \times 6 \times 50$ mm^3 were made with a Zwick 5102 pendulum-type testing machine according to ISO 179-1993(E).

The morphology of the fractured surfaces of the specimens was investigated with a JEOL JSM-6335F field emission scanning electron microscope (FESEM). The

Table 1
Commercial compatibilizers in PE/ATH and PE/MH blends

Compatibilizer	Functionality	Content of functionality (wt%)	Grade	Manufacturer
E/BA	Butyl acrylate	7.0	LE 6471	Borealis Polymers
E/BA/MAH	Maleic anhydride	0.5 (BA 5.4)	ME 0420	Borealis Polymers
E/GMA	Glycidyl methacrylate	8.0	L Lotader® AX 8840	Atofina
PE-*g*-AA	Acrylic acid	6.0	Polybond® 1009	Uniroyal Chemicals

Table 2
Polymerizations performed with metallocene catalyst and properties of the copolymers

Comonomer	Catalyst	$n_{com.}$ (mmol)	n_{cat} (μmol)	Al/Zr	$n_{Al}/n_{com.}$	T_p (°C)	P_{eth} (bar)	t_p (min)
ROH1	$Et(Ind)_2ZrCl_2/MAO$	15.0	5.0	12 000	4.0	60	1.5	40
ROH2	$Et(Ind)_2ZrCl_2/MAO$	7.5	5.0	9000	6.0	60	1.5	40
ROH3	$Me_2Si(2\text{-}MeInd)_2\text{-}ZrCl_2/MAO$	7.5	10.0	3000	4.0	60	1.5	30
ROH4	$Et(2\text{-}(t\text{-}BuMe_2SiO)\text{-}Ind)_2ZrCl_2/MAO$	15.0	2.0	30 000	4.0	60	1.5	20
RCOOH1	$Et(Ind)_2ZrCl_2/MAO$	10.0	10.0	8000	8.0	45	1.2	54
RCOOH2	$Et(Ind)_2ZrCl_2/MAO$	15.0	5.0	18 000	6.0	60	1.5	35
Copolymer	A (kg/(mol Zr h))	M_w (g/mol)	M_w/M_n	T_m (°C)	ΔH (J/g)	Content of functionality (mol%)	Content of functionality (wt%)	
PE-*co*-OH1	2900	75 000	2.6	126	153	1.02	5.9	
PE-*co*-OH2	6400	124 000	2.8	130	159	0.30	1.8	
PE-*co*-OH3	2500	244 000	3.4	129	131	0.30	1.8	
PE-*co*-OH4	24 000	80 000	2.5	128	156	0.80	4.7	
PE-*co*-COOH1	1700	147 000	2.9	127	140	0.31	2.0	
PE-*co*-COOH2	6400	130 000	2.9	129	144	0.35	2.2	

specimens were fractured after cooling in liquid nitrogen, and the fractured surfaces were sputter-coated with gold under argon. The electron micrographs were taken using an acceleration voltage of 5.0 kV.

Melting and crystallization behavior were studied with a differential scanning calorimeter (DSC) Mettler Toledo DSC821^e under nitrogen. The rates of cooling and reheating were 10 °C/min and the temperature range varied from 25 to 160 °C.

Dynamic mechanical analysis (DMA) measurements were performed with a PerkinElmer DMA-7. The experiments were carried out using the three-point-bending geometry over a temperature range of -120 to 100 °C at a rate 4 °C/min under nitrogen flow. All specimens were scanned at a frequency of 1 Hz. The rectangular specimen dimensions were $18 \times 4 \times 1.5$ mm^3.

A cone calorimeter was used for the flammability characterization under a heat flux of 35 kW/m^2 according to ISO 5660. The cone calorimeter is basically an oxygen consumption calorimeter, which measures the responses of materials when exposed to different thermal irradiances; the method is based on the principle that for a range of materials the net heat of combustion is proportional to the amount of oxygen required for combustion.

3. Results and discussion

3.1. Mechanical properties

Table 3 lists the tensile modulus, tensile strength, elongation at break, and Charpy impact strength of notched specimens for PE/ATH and PE/MH (60/40) blends with compatibilizer additions of 2, 5, and 10 wt%. An addition of 40 wt% of ATH or MH produced a clear increase in the tensile modulus of polyethylene (Fig. 1). Concurrently, however, the samples became much more brittle as can be seen in the low values of Charpy impact strength and elongation at break (Fig. 2). Because a usual method to compensate loss in toughness is to apply a coating [1,17,18], blends of polyethylene with stearic acid treated ATH or MH were also prepared. As expected, these blends showed a moderate improvement in toughness, but at the cost of stiffness and strength.

When the stearic acid treatment was replaced by an addition of functionalized polyethylene in the blending step, pronounced improvement was achieved in both stiffness and toughness (Figs. 1 and 2). Thus, the longer organic chain was shown to be beneficial to the mechanical properties of the composite. Of the commercial compatibilizers, in which the functionalities were butyl acrylate, maleic anhydride, epoxy, and carboxylic acid, the polyethylenes containing butyl acrylate as compatibilizer gave the highest values of impact strength and elongation at break. Acrylic acid functionalized polyethylene improved the impact strength and elongation at break of the composites with untreated

Table 3
Tensile modulus (E), tensile strength (σ), elongation at break (ε_b), and Charpy impact strength of notched specimens of PE/ATH and PE/MH composites with compatibilizer addition of 2, 5, or 10 wt%

Composite	E (MPa)	SD	σ (MPa)	SD	ε_b (%)	SD	Charpy impact strength (notched) (kJ/m^2)	Charpy impact strength (notched) SD
PE	61	3	16.6	0.9	116	10	NB	–
+ATH	141	6	16.1	0.5	49	6	11	1
+ATH(SA)	126	4	16.0	1.7	54	4	17	2
+ATH + E/BA	135	12	15.9	2.4	65	13	42	2
+ATH + E/BA/MAH	136	6	17.6	1.1	50	4	43	2
+ATH + E/GMA	134	8	16.0	0.8	47	6	41	4
+ATH + PE-*g*-AA	206	7	17.4	0.3	51	8	24	4
+ATH + PE-*co*-OH1	152	7	18.5	1.5	56	4	40	3
+ATH + PE-*co*-COOH1	184	9	17.9	2.3	57	20	28	5
+ MH	193	12	15.2	1.7	47	4	13	3
+MH(SA)	150	5	14.2	0.6	53	4	29	3
+MH + E/BA	145	5	17.4	1.6	49	4	35	5
+MH + E/BA/MAH 2%	183	14	17.7	1.2	53	10	28	2
+MH + E/BA/MAH 5%	168	11	19.0	1.1	45	7	36	2
+MH + E/BA/MAH	172	6	19.2	1.3	47	6	35	2
+MH + E/GMA	153	3	16.5	0.5	42	4	28	3
+MH + PE-*g*-AA	220	8	18.5	0.5	49	5	23	2
+MH + PE-*co*-OH2	235	7	22.2	2.4	50	3	30	3
+MH + PE-*co*-OH3 5%	208	5	21.2	1.0	41	3	31	4
+MH + PE-*co*-OH3	229	6	23.3	1.2	42	6	34	3
+MH + PE-*co*-OH4	210	8	20.7	1.3	49	6	35	3
+MH + PE-*co*-COOH2	206	9	18.8	1.6	43	7	27	3

fillers, but not as much as the other functionalized polyethylenes. Even with stearic acid treatment, the toughness of the composites was better. The stiffness was on a much higher level, however, with acrylic acid functionalized polyethylene than with other commercial compatibilizers, as can be seen in Fig. 1.

The copolymers we prepared with metallocene catalysts improved the mechanical properties as depicted in Figs. 1 and 2. Toughness was as good as achieved with the best commercial compatibilizers and values of tensile modulus and strength were higher than with effective commercial compatibilizers. Hydroxyl functionalized polyethylenes seemed to be more efficient in improving the mechanical properties than carboxylic acid functionalized polyethylene. Especially with ATH, the effect of carboxylic acid functionalized polyethylene was similar to that of acrylic acid functionalized polyethylene in generating very high tensile modulus, but it did not bring about as substantial an increase in impact. Hydroxyl functionalized polyethylenes with different molecular weights and amounts of functionality and crystallinity were tested as compatibilizers in the composite of polyethylene with MH. All improved the toughness, as expected, and no dependence of the properties of the composites on those of the compatibilizers was found. Molecular weight and the content of functionality were on

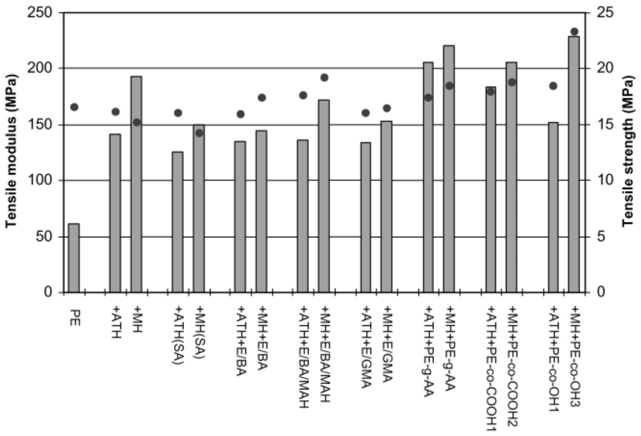

Fig. 1. Tensile modulus (columns) and tensile strength (points) of PE/ATH and PE/MH composites with compatibilizer additions of 10 wt%.

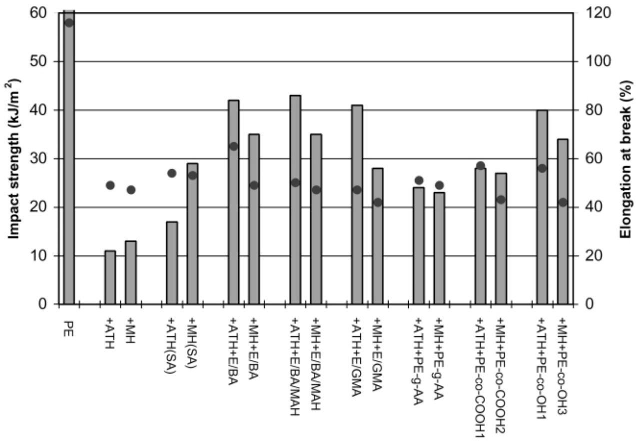

Fig. 2. Charpy impact strength of notched specimens (columns) and elongation at break (points) of PE/ATH and PE/MH composites with compatibilizer additions of 10 wt%.

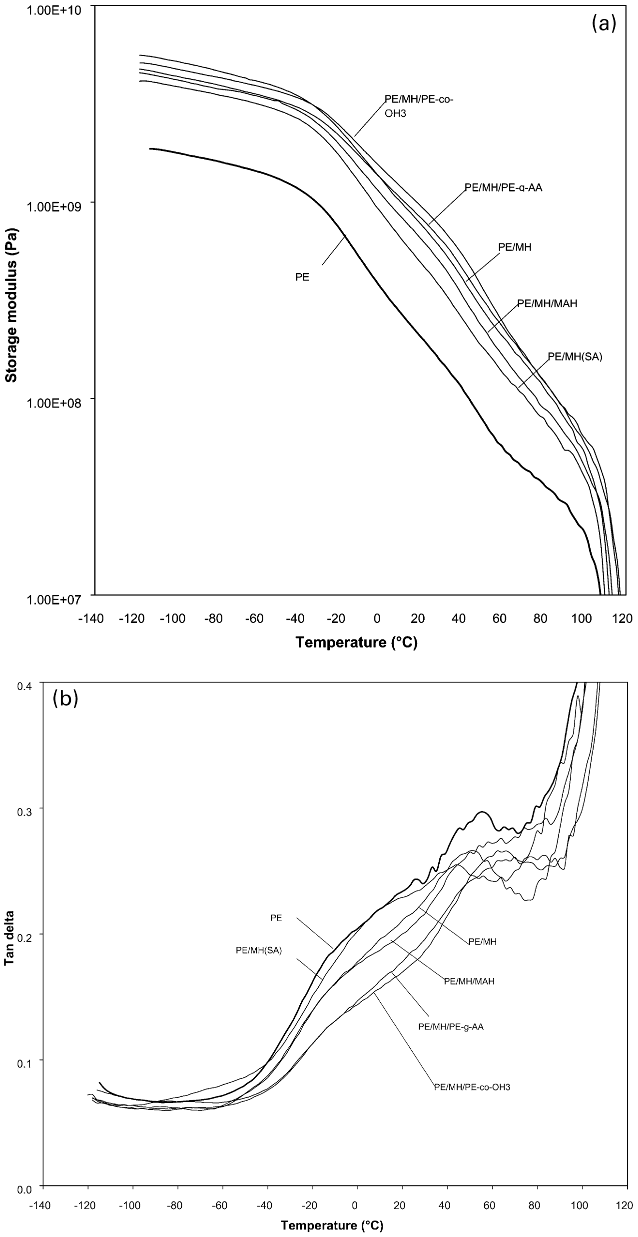

Fig. 3. (a) Storage modulus E' and (b) tan δ curves of neat polyethylene (PE) and its composites PE/MH, PE/MH(SA), PE/MH/(E/BA/MAH), PE/MH/PE-*g*-AA and PE/MH/PE-*co*-OH3.

adequate level so that there was enough functionality to interact with the hydroxyl groups of the fillers, and at the same time, chains were long enough to be able to entangle with chains of the polyethylene matrix. Thus, tensile modulus and strength were also very high with all hydroxyl-functionalized polyethylenes.

The amount of compatibilizer needed to improve the mechanical properties was evaluated with additions of E/BA/MAH or PE-*co*-OH3 to the PE/MH composite. Properties achieved with an addition of 10 wt% could also be achieved with an addition 5 wt%, but an addition of 2 wt% appeared to be insufficient.

Differences in the effects of ATH and MH on the

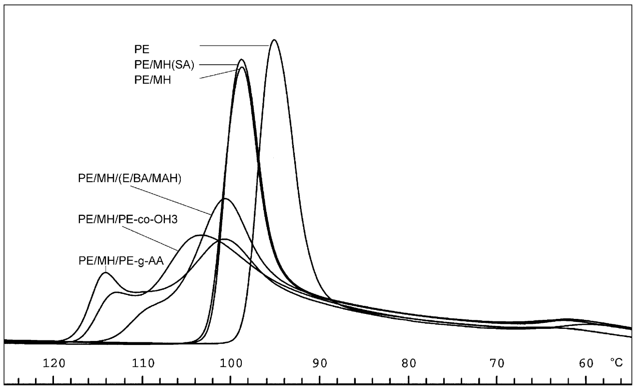

Fig. 4. Cooling thermograms of neat PE and uncompatibilized and some compatibilized PE/MH composites.

mechanical properties of polyethylene composites are readily seen in Figs. 1 and 2. The effect of stearic acid treatment was much more pronounced in PE/MH composite than in PE/ATH composite. The increase in impact strength due to compatibilizers was not as great with MH as with ATH, but the tensile modulus and strength were clearly higher. The highest values in impact strength were achieved with ATH and polymeric compatibilizers.

3.2. Dynamic mechanical analysis

DMA was performed for neat polyethylene and its composites to obtain further information on mechanical properties and molecular motions. DMA is a method that measures the stiffness and mechanical damping of a cyclically deformed material as a function of temperature. Identification of the glass transition temperature (T_g) is one of the most common uses of DMA and generally T_g is determined as a maximum of tan *delta* curve and seen as a drop in storage modulus curve. When observed transitions in polymer are more than one, it is customary to label relaxation transitions as α, β, γ, etc. in alphabetical order with decreasing temperature. According to literature [19,20] neat polyethylene has three relaxations, located in the vicinity of − 120 °C (γ), 0 °C (β), and 70–80 °C (α). In this work (Fig. 3(a) and (b)) obvious drop in the storage modulus (E') and transitions in tan *delta* curve at 0 and at 70–80 °C can be seen, whereas because of starting temperature − 120 °C, γ relaxation could only be seen as a very small change in curve of E'.

The filler effect, expected increase in E', was clearly observed when ATH or MH was added to polyethylene. As noted above the composites of stearic acid treated ATH and MH showed improvement in toughness but not in strength, and similar behavior was seen in the DMA measurements, where the E' value of PE/MH(SA) was clearly higher than that of the neat polyethylene but the lowest of all E' values for composites. Values of storage modulus were highest for composites with an addition of 10 wt% of functionalized

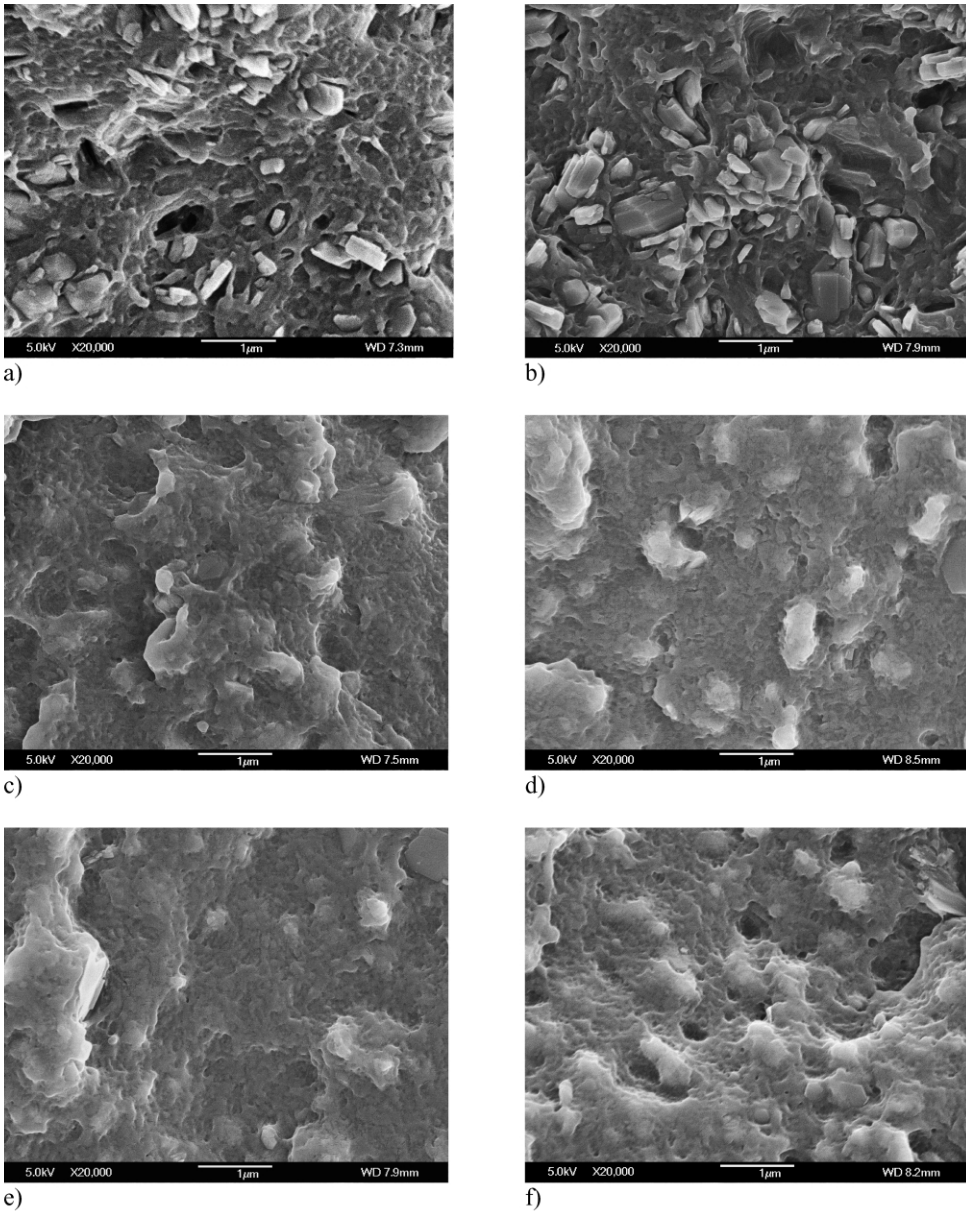

Fig. 5. SEM micrographs of PE/ATH composites (× 20 000). (a) PE/ATH (60/40), (b) PE/ATH(SA) (60/40), (c) PE/ATH/(E/BA/MAH) (50/40/10), (d) PE/ATH/PE-*g*-AA (50/40/10), (e) PE/ATH/PE-*co*-OH (50/40/10), (f) PE/ATH/PE-*co*-COOH (50/40/10).

polyethylenes, and at 25 °C the order correlated with the values of the tensile modulus.

Fig. 3(b) shows the three relaxations presented as tan δ curves. The β peak at 0 °C has been associated with the relaxations of side groups or short branch points and the α peak at 70–80 °C with vibrational motion and reorientation within the crystals. The α relaxation has also been interpreted as relaxation of the constrained molecules with reduced mobility located near the crystallites. The third peak of polyethylene would be near −120 °C and that peak has been assigned to chain relaxation in the amorphous phase [21,22].

Because the β relaxation is a dominant process in low density polyethylene (LDPE) but an insignificant one in high density polyethylene (HDPE), it has been associated with the motion of side chains. The long-chain branching interferes with the formation of tie molecules and crystalline growth, resulting in smaller and thinner crystallites with more and weaker crystal interfaces, and furthermore it decreases the improvements obtained in mechanical properties, as with PE/MH/(E/BA/MAH). In DMA measurements, PE/MH/PE-*co*-OH3 seems to be closest in behavior to HDPE, and evidently, because of less branching it has larger and more perfect crystallites as well as thicker lamellae with entanglements leading to better interfacial adhesion and to better mechanical properties. In the fillers treated with stearic acid, the organophilic nature of the filler is modified, making it more easily dispersible, and particles that are well dispersed generally rise to better properties. Change in the physical

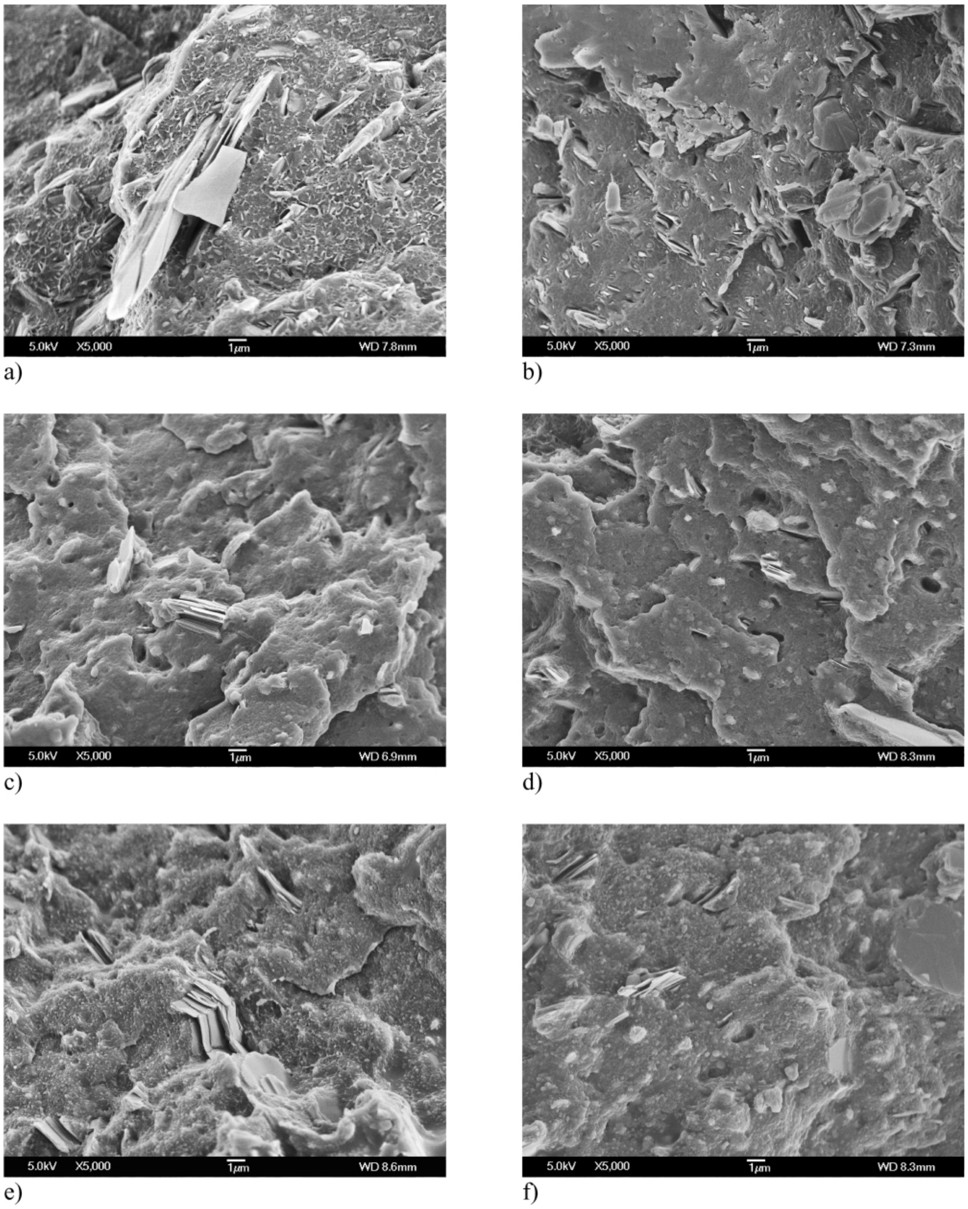

Fig. 6. SEM micrographs of PE/MH composites (×5000). (a) PE/MH (60/40), (b) PE/MH(SA) (60/40), (c) PE/MH/(E/BA/MAH) (55/40/5), (d) PE/MH/(E/BA/MAH) (50/40/10), (e) PE/MH/PE-*g*-AA (50/40/10), (f) PE/MH/PE-*co*-OH3 (50/40/10).

state of the matrix surrounding the treated filler hinders molecular motion and this may be one of the factors causing broadening of peak intensity observed for the β- and especially the α-relaxation. Storage modulus as well as impact strength improved with the treated fillers, owing to better dispersibility and decreased interfacial tension, but improvement in tensile modulus was not achieved owing to the weak interactions between filler and matrix.

As can be seen in Fig. 3(b), the incorporation of functionalized polyethylene seems to lead to a reduction in magnitude of peak intensity for the β-relaxation (0 °C), while the position of the peak remains virtually unchanged. This result may suggest that incorporation does not significantly influence the crystallization or percentage of crystallinity because such processes are related to changes in peak location [21].

In DMA analysis an increase in E' and a lowering of the damping factor, as well as broader peaks indicate improved interfacial adhesion and improved interfacial adhesion hinders further molecular motion, leading to a stiffer and tougher material. The best results in these measurements were obtained with our hydroxyl functionalized polyethylenes prepared with metallocene catalysts.

3.3. *Differential scanning calorimetry*

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 (10 wt%) further changed this. No clear difference in melting or crystallization enthalpies could be linked, which indicates that the influence of the compatibilizer on the degree of crystallinity was not significant. Crystallization temperatures, on the other hand, changed slightly as shown in Fig. 4 for PE/MH composites. An addition of 40 wt% of ATH or MH to the polyethylene increased the crystallization temperature (T_c) by about 3 °C and the onset temperature of crystallization (T_{oc}) 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.

3.4. Morphology

Morphologies of the uncompatibilized and some compatibilized composites of PE with ATH and MH are shown in Figs. 5 and 6. Comparison of the filler particles reveals that MH is platy in structure and has a fairly broad size distribution, whereas ATH particles are smaller and much more homogeneous in size. The blends without compatibilizer depicted in Figs. 5(a) and 6(a) show clearly that the particles are not attached to the matrix. Similarly, when the particles are treated with stearic acid, debonding occurs between the particles and the matrix (Figs. 5(b) and 6(b)). An addition of 10 wt% of any of the polymeric compatibilizers improves the adhesion so much that the fracture mechanism changes from adhesion to cohesion failure. The particle size distribution is more homogeneous in ATH and as can be seen in Fig. 5(c)–(f) all the particles are coated to yield a smooth fracture surface in the composite. Particle size distribution was broader in MH, and then smaller particles, i.e. particles up to 1 or 2 μm, were uniformly coated. Larger particles, too, were better attached to the matrix, and during fracture the filler was more brittle than the interface between the filler and the matrix. Instead of pulling out of the matrix the filler particles split. With E/BA/MAH and PE-*co*-OH, improved adhesion was gained even with 5 wt% addition of compatibilizer as was evident in both morphology studies (Fig. 6(c)) and mechanical properties (Table 3). In view of the change in fracture mechanism with compatibilization, if further improvement in mechanical properties is required, attention should be paid to the choice of the matrix material.

3.5. Cone calorimetry

Measurements with a cone calorimeter were done to check for changes in flammability properties when untreated or stearic acid treated filler or both filler and polymeric compatibilizer were added to polyethylene. Measurements were done with both ATH and MH and the trends were found to be similar. Times to ignition and heat release rates (HRR) for neat polyethylene with MH and its composites are shown in Fig. 7. Neat polyethylene was ignited in 57 s and the HRR was as high as 1200 kW/m^2 at maximum. An 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 composites with polymeric compatibilizer 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 obtained curves were very similar those in HRR curves. It can be concluded that the flammability properties of the composites are not negatively affected by the addition of polymeric compatibilizers as adhesion promoters.

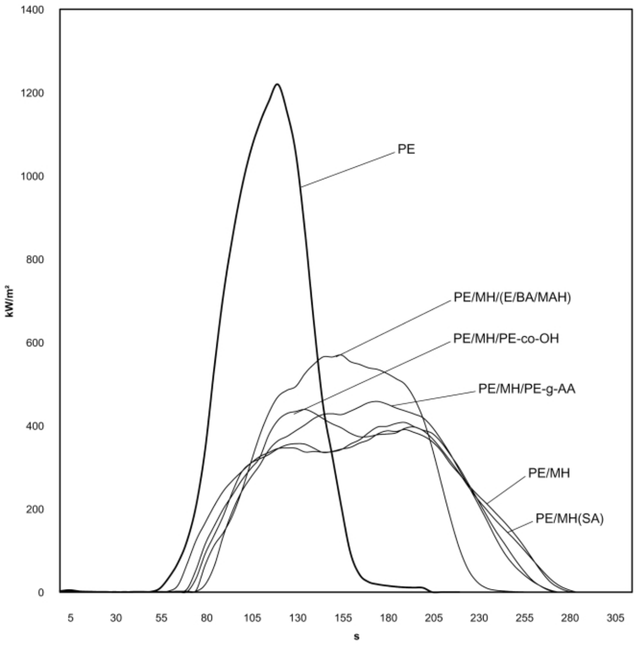

Fig. 7. Heat release rate of neat polyethylene and its composites with MH.

4. Conclusions

Study was made of the compatibilization of composites of polyethylene with ATH or MH hydroxyl or carboxylic acid functionalized copolymers prepared with metallocene catalysts and with commercial butyl acrylate, maleic anhydride, epoxy and acrylic acid functionalized polyethylenes. Comparison was made with composites of polyethylene with stearic acid treated ATH and MH. Adhesion of PE/ATH and PE/MH composites was dramatically increased by compatibilization, as seen in morphology studies in the changed fracture mechanism. The adhesion fracture observed in composites prepared without polymeric compatibilizers whether treated with stearic acid or not, was changed to cohesion failure with the addition of any of the functionalized polyethylenes. This improvement in adhesion was particularly reflected in the mechanical properties, and improvement in both stiffness and toughness was best achieved with our functionalized copolymers prepared with metallocene catalysts. According to the cone calorimetry tests, the improvements in flammability properties achieved when ATH or MH are added as fillers to polyethylene are preserved when polymeric compatibilizers are used as adhesion promoters.

Acknowledgements

Kimmo Hakala, Sami Sneck, Santeri Paavola and Tanja Seraidaris are warmly thanked for the preparation and characterization of functionalized polyethylenes prepared with metallocene catalysts. Jaakko Iisalo is thanked for the preparation and characterization of some of the composites. We are further grateful to Kari Lounatmaa from the Laboratory of Electronics Production Technology at Helsinki University of Technology for the scanning electron micrographs, and to Jari Huhtala and Riitta Teimola from Borealis Polymers for the cone calorimeter measurements. Funding for this project was received from the National Technology Agency (TEKES).

References

[1] Pritchard G, editor. Plastics additives, an A–Z reference. London: Chapman & Hall; 1998. p. 633.
[2] Wypych G. Handbook of fillers, 2nd ed. Toronto: ChemTec Publishing; 1999. p. 890.
[3] Sperling LH. Polymeric multicomponent materials. New York: Wiley; 1997. p. 397.
[4] Rothon R. Particulate-filled polymer composites. Bath: Longman Scientific and Technical; 1995. p. 375.
[5] Hausmann K, Flaris V. Polym Comp 1997;5:113–9.
[6] Jančář J, Kucera J. Polym Engng Sci 1990;30:714–20.
[7] Rahma F, Fellahi S. Polym Comp 2000;21:175–86.
[8] Mai K, Li Z, Qiu Y, Zeng H. J Appl Polym Sci 2001;80:2617–23.
[9] Hornsby PR, Watson CL. J Mater Sci 1995;30:5347–55.
[10] Chiang WY, Hu CH. Composites: part A 2001;32:517–24.
[11] Jančář J. J Mater Sci 1989;24:4268–74.
[12] Fang Z, Hu Q. Angew Makromol Chem 1999;265:1–4.
[13] Strålin A, Hjertberg T. J Adhes 1993;41:51–80.
[14] Ahjopalo L, Löfgren B, Hakala K, Pietilä L-O. Eur Polym J 1999;35: 1519–28.
[15] Anttila U, Hakala K, Helaja T, Löfgren B, Seppälä J. J Polym Sci, Part A: Polym Chem 1999;37:3099–108.
[16] Hakala K, Helaja T, Löfgren B. J Polym Sci, Part A: Polym Chem 2000;38:1966–71.
[17] Haworth B, Raymond CL, Sutherland I. Polym Engng Sci 2001;41: 1345–64.
[18] Liauw CM, Rothon RN, Lees GC, Dumitru P, Iqbal Z, Khunova V, Alexy P. Functional and effect fillers for reinforcing polymer systems, 13–15th September, 2000. Berlin, Germany (Intertech, USA).
[19] Nielsen LE, Landel RF. Mechanical properties of polymers and composites, 2nd ed. New York: Marcel Dekker; 1994. p. 557.
[20] Scobbo JrJJ. In: Paul DR, Bucknall CB, editors. Thermomechanical performance of polymer blends in polymer blends. New York: Wiley; 2000. p. 337–56.
[21] Bikiaris D, Matzinos P, Prinos J, Flaris V, Larena A, Panayiotou C. J Appl Polym Sci 2001;80:2877–88.
[22] Premphet K, Horanont P. Polymer 2000;41:9283–90.