Impact-Modified Poly(styrene-*co*-acrylonitrile) Blends Containing Both Oxazoline-Functionalized Poly(ethene-*co*-1-octene) Elastomers and Poly(styrene-*co*-maleic anhydride) as Compatibilizer

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ABSTRACT: Blends of a poly(styrene-*co*-acrylonitrile) (SAN) with poly(ethene-*co*-1-octene) rubber (EOR) were investigated. An improved toughness–stiffness balance was obtained when adding as a compatibilizer a blend consisting of oxazoline-functionalized EOR, prepared by grafting EOR with oxazoline-functional maleinate, and poly(styrene-*co*-maleic anhydride) (SMA), which is miscible with SAN. Enhanced interfacial adhesion was evidenced by the improved dispersion of the EOR in the SAN matrix and the reduced glass transition temperature of the dispersed EOR phase. Morphology studies using transmission electron microscopy revealed formation of an interphase between the matrix and the rubber particles. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1685–1695, 1999

Key words: SAN; oxazoline; blend; rubber; metallocene; reactive blending; SMA

INTRODUCTION

An important objective in the development of engineering polymers, such as polystyrene (PS) and poly(styrene-*co*-acrylonitrile) (SAN), is to improve simultaneously the stiffness and impact strength.[1] Frequently, impact modification is achieved by blending SAN together with SAN-grafted polybutadiene rubber to form ABS. However, the addition of olefinically unsaturated rubber accounts for the lower environmental stability of ABS, especially with respect to oxidative deg-

radation. This drawback limits the application of such blends. Therefore, saturated elastomers are of special interest in SAN blend formation.

During the 1980s, novel "single-site"-based catalyst systems emerged which produce ethene/1-olefin copolymers covering the entire feasible comonomer composition range without sacrificing uniform comonomer incorporation, narrow molecular weight distribution, and high molecular weights. Ethene/1-octene copolymers (EOR) with a 1-octene content exceeding 10 mol % are attractive rubbers and thermoplastic elastomers with the glass transition temperature below −40°C. Such ethene/1-octene became known as flexomers or plastomers, respectively.[2,3] Due to their pronounced incompatibility with polar polymers, as evident from their high values of interfacial tension,[4] EOR requires a compatibilizer during melt processing in blends with SAN. Otherwise, the

high interfacial tension between the different phases leads to a large size of the dispersed rubber phase. Upon exposure to small mechanical stresses, noncompatibilized blends exhibit premature mechanical failure, that is, brittle behavior. Compatibilizers can be introduced by adding special block or graft copolymers as interfacial coupling agents.[5–8] Moreover, reactive blending can be applied to achieve interfacial adhesion *in situ* during the processing of multiphase materials.[9–11]

To use EOR for reactive processing, it is necessary to introduce reactive groups at the EOR backbone. A convenient route for the functionalization of polyolefins, that is, isotactic polypropene (PP) or polyethene (PE), is melt free-radical grafting of maleic anhydride (MA).[10–15] Also methacrylates, for example, glycidyl methacrylate, are used for free-radical grafting during extrusion.[15] Maleinates, bearing another additional functional group, can be employed for grafting. Recently, it was shown that ricinoloxazoline maleinate (OXA-MAL) can be grafted successfully onto the polymer backbone of saturated polyolefins by melt free-radical grafting processes.[16–19] For example, Seppälä and coworkers[18,19] prepared oxazoline-functionalized PP (PP-*g*-OXA) via grafting of OXA-MAL. Processing PP/PBT blends in the presence of PP-*g*-OXA afforded improved impact strength under retention of the stiffness.

Oxazoline-functionalized EOR should be readily available using the same reaction conditions as described for PP. However, PS and SAN do not contain any functional groups able to react with oxazoline-functional EOR. Therefore, addition of a third component, capable of reacting with the oxazoline-functionalized EOR, and at the same time being miscible with SAN, is needed as an additional compatibilizer. The addition of poly-(styrene-*co*-maleic anhydride) (SMA) to SAN provides the possibility of reactive blending due the anhydride functionality. It is known that SMA is miscible with SAN if the MA content in SMA and the acrylonitrile (AN) content in SAN are very similar.[20–30] The compatibility of SAN and SMA was already used in reactive extrusion of SAN/polyamide (PA) blends which were compatibilized using SMA, which is capable of reacting with the amine end groups of PA[31,32] and is miscible with the SAN matrix at the same time.

It is proposed that copolymers containing pendant oxazoline groups, such as poly(styrene-*co*-isopropenyloxazoline), are able to react with MA-

Figure 1 Proposed reaction mechanisms of SMA with 2-substituted 1,3-oxazolines: (a) water-induced ring opening of MA generating carboxylic acid groups, (b) followed by reaction of the carboxylic acid groups with 1,3-oxazolines, (c) addition of the oxazoline group to MA forming a bicyclic adduct, and (d) ring opening of bicyclic adduct by water.

grafted polymers.[16,33–38] However, reaction of MA-containing copolymers with oxazolines has not been studied extensively.[35,36] The mechanism of the reaction of oxazolines with MA copolymers, such as SMA, is not fully understood. There is some literature describing the reaction of 1,3-oxazolines with MA, but only model systems of monomeric anhydrides were studied. The reaction between 2-substituted 1,3-oxazolines and monomeric anhydrides is believed to proceed as apolyaddition[39–49] via a zwitterion mechanism.[50] The reaction of anhydride-containing copolymers with polymeric oxazolines, however, may involve water-induced ring opening of MA, thus generating carboxylic acid groups, followed by the formation of esteramide as depicted in Figure 1(a,b).[36,37] Another proposed mechanism [Fig. 1(c)] involves the addition of the oxazoline group to MA, forming a bicyclic adduct. This adduct might undergo ring opening in the presence of water [Fig. 1(d)], forming an amide–ester.[35] In both proposed mechanisms, the coreaction of water is postulated.

The aim of this article was to study the functionalization of EOR with OXA-MAL by free-rad-

Table I Abbreviations and Physical Properties of the Polymers Used

Polymer	Abbreviation	Comonomers	Content (wt %)	M_w (g/mol)	M_w/M_n	T_g/T_m[a] (°C)
Luran 358N poly(styrene-*co*-acrylonitrile)	SAN	Styrene, acrylonitrile	75 25	160,000	2.2	110
Dylark 332/80 poly(styrene-*co*-maleic anhydride)	SMA	Styrene, maleic anhydride	84.7 15.3	180,000	2.1	105
Engage EG 8150 poly(ethene-*co*-1-octene)	EOR	Ethene, octene	75 25	153,500	2.1	−42/61
LOXAMID VEP 8515 ricinoloxazoline maleinate	OXA-MAL	—	—	480		

[a] T_g determined by DSC measurements (heating rate 10 K/min).

ical melt grafting in order to produce oxazoline-functionalized EOR (EOR-*g*-OXA). The melt reaction of the MA groups of SMA and 2-substituted 1,3-oxazolines should proceed fast enough to be used for reactive processing using EOR-*g*-OXA. Reactive melt blending of EOR-*g*-OXA with SAN/SMA is expected to afford new multiphase polymers based upon SAN and EOR, exhibiting controlled morphology development and improved impact properties.

EXPERIMENTAL

Materials

All polymers used in this study and their characteristics are shown in Table I. SAN (Luran® 358N) was supplied by BASF AG, SMA (Dylark 332/80) was supplied by Arco Chemicals, and EOR (Engage™ EG 8150) was supplied by Dow Chemical. The grafting reagent ricinoloxazoline methylmaleinate Loxamid VEP 8515, abbreviated OXA-MAL, was supplied by Henkel KGaA. The content of the oxazoline groups was 2.08 mol/kg as determined by titration. The radical initiator di-*tert*-butylperoxide (DTBP) was purchased from Fluka. Irganox® 1010 (0.2 wt %)/Irgafos® 168 (80 : 20 wt %) were added as stabilizers during reactive processing. However, grafting was performed in the absence of additional stabilizers. 1,4-bis(1,3-Oxazolin-2-yl)butane (OXA-OXA) was synthesized according to literature procedures.[51]

Preparation of Oxazoline-functionalized EOR

Preparation of oxazoline-functionalized EOR was performed according to procedures described for polyolefins[16] and already applied to PP.[18,19] EOR (51.7 g, density of 0.868 g/cm^3) was fed into a Haake Rheomix 90 twin-screw kneader equipped with a 60-mL mixing chamber which was preheated at 200°C and operated at 60 rpm. EOR was molten for 1.5 min. Then, 5.2 g of a mixture of OXA-MAL/DTBP (ratio 95 : 5 wt %) was added within 0.5 min. After a reaction time of 5 min (total mixing time was 7 min), the sample was quickly recovered and quenched between cooled metal plates. The product is abbreviated EOR-*g*-OXA.

Determination of Grafting Yield

The grafting yield (GY) was determined using FTIR as described elsewhere.[19] The signal at 1668 cm^{-1} was attributed to a complex mode involving C=N stretching and oxazoline bending. An additional contribution to the intensity of this signal is the internal double bond of the ricinol. The signal at 1728 cm^{-1} was attributed to the ester groups in EOR-*g*-OXA. Because of the low intensity of both signals, the complete signal between 1600 and 1800 cm^{-1} was integrated and treated as the characteristic signal for grafted oxazoline of EOR-*g*-OXA. The signal at 2960 cm^{-1}, C—H vibrations of the polyolefin was taken as the reference.

Preparation of Melt Blends

All blends were prepared under identical mixing and molding conditions. The elastomer weight fraction was varied between 0 and 25 wt %. Reactive blending was performed in the kneader preheated at 225°C and operated at 90 rpm. The kneader was always filled with 45 mL of the poly-

mer. Typically, SAN/SMA was molten together with the stabilizers for 1.5 min. Then, the modified (EOR-*g*-OXA) or the nonmodified elastomer (EOR) was added. After a reaction time of 5.5 min (total mixing time was 7 min), the sample was quickly recovered and quenched between cooled metal plates. The melt temperature and torque were continuously recorded during the mixing period on a Haake Rheocord, Model 5000. Sheets of 2 mm thickness were prepared by compression molding in an evacuated melt press (Schwabenthan Polystat 100).

Characterization

FTIR spectra were recorded using a Bruker IFS 88 spectrometer. For titration analysis of the oxazoline functionality, OXA-MAL was dissolved in $CHCl_3/CH_3CO_2H$ and titrated with $0.1N$ $HClO_4/$ AcOH using a Mettler DL25. Size-exclusion chromatography (SEC) was performed on a Knauer Mikrogelset A14 using $CHCl_3$ as a solvent, calibrated with PS standards. Differential scanning calorimetry measurements were performed on a Perkin–Elmer DSC 7 at a heating rate of 10 K/min.

The morphology of the blends was determined using an environmental scanning microscope (ESEM) Model 2020 of ElectroScan Corp. To obtain more detailed information, the fracture surfaces of the cryofractured samples were sputtered with gold. The acceleration voltage was 25 kV.

TEM measurements were done with a Zeiss CEM 902 transmission electron microscope applying an acceleration voltage of 80 kV. The samples were cut with an ultramicrotome (Ultracut E, Reichert & Jung, equipped with a diamond knife) at room temperature. Ultrathin sections of approximately 70 nm were stained with RuO_4 prepared from 10 mg $RuCl_3$ and 5 mL of 10 wt % NaOCl solution over the gas phase.

Glass transition temperatures were measured by dynamic mechanical analysis on a Rheometrics solids analyzer RSA II at 1 Hz and a heating rate of 2 K/min using a dual cantilever geometry ($50 \times 6 \times 2$ mm) and a strain of 0.2%.

Mechanical Tests

Tensile properties were measured on an Instron (Model 4202) tensile machine according to the DIN 53455 standard procedure using a test specimen of 2 mm thickness and a crosshead speed of 10 mm/min. Notched Izod impact strength values

Figure 2   Torque–time relationship ($T = 225°C$, 90 rpm) for (a) pure SMA and (b) SMA with addition of 1 wt % OXA-OXA.

were determined on notched samples according to ISO 180/1A using a test specimen of $60 \times 10 \times 2$ mm. The average standard deviations of the Young's modulus and tensile stress were approximately 5%; of impact strength, 10%; and of elongation at break, 30%. A minimum of five specimens was tested for each blend composition and the average value is reported. All tests were performed at ambient temperature ($23 \pm 2°C$).

RESULTS AND DISCUSSION

Model Reaction Between SMA and Oxazolines

To verify that the reaction of the oxazoline group with MA of the SMA proceeds fast enough to be suitable for reactive blending, two test series were performed in the kneader. In series I, the torque of the melting of pure SMA and SMA with subsequent addition of 1 wt % OXA-OXA after 2.5 min was recorded ($T = 225°C$, 90 rpm) and is depicted in Figure 2. In Figure 2(a), it can be seen that the melting of SMA leads to a constant decrease in torque. Addition of 1,4-bis(1,3-oxazolin-2-yl)butane (OXA-OXA) to the SMA melt causes a reduced torque which is due to the melting of OXA-OXA followed by an increase in torque as depicted in Figure 2(b). Reaction between MA and OXA-OXA leads to fast network formation. This provides good evidence that the reaction of 1,3-oxazolines and SMA proceeds fast enough to be useful in reactive blending applications.

Figure 3 Torque–time relationship (T = 225°C, 90 rpm) for (a) pure SMA, (b) SAN with addition of 2 wt % OXA-MAL, and (c) reactive system SMA with addition of 2 wt % OXA-MAL.

The melting of SAN with a subsequent addition of 2 wt % OXA-MAL after 2.5 min and the melting of SMA with subsequent addition of 2 wt % OXA-MAL after 2.5 min was investigated at identical temperatures. Figure 3(b) shows the addition of the oily OXA-MAL to SAN, leading to a small decrease in torque and a slow regaining of a torque value very similar to that of pure SMA, which is depicted in Figure 3(a). Addition of OXA-MAL to SMA, however, gives a short drop followed by an increase in torque due to both the reaction of oxazoline with the MA functionality of SMA and the grafting of the polymer with the maleinate group of OXA-MAL [Fig. 3(c)].

Reactive Blending of the Binary Blend SMA/EOR-*g*-OXA

For the first step, EOR was modified by melt free-radical grafting with OXA-MAL. The grafting yield (GY), that is, the amount of grafted OXA-MAL with respect to OXA-MAL in the feed, was GY = 0.45. This is in good agreement with other results[19] and equivalent to about 94 μmol/g oxazoline groups in EOR-*g*-OXA. The material was used without further purification, that is, there is still a certain amount of ungrafted OXA-MAL.

To show that SMA and EOR-*g*-OXA can be used successfully in reactive processing, this system was initially studied without any addition of SAN. Two different blend compositions were prepared (80 : 20 and 20 : 80) for the nonreactive

(SMA/EOR) and the reactive system (SMA/EOR-*g*-OXA). The torque values of these systems were recorded as a function of kneading time. For both compositions, the recorded torque of the reactive system SMA/EOR-*g*-OXA was higher than for the nonreactive system SMA/EOR.

Furthermore, the morphology of the resulting blends after a mixing time of 7 min at 225°C was studied by ESEM. Figure 4 depicts the fracture surfaces of different blend systems at composition ratios of 80 : 20 and 20 : 80 wt %. Figure 4(a) shows the surface of the nonreactive system SMA/EOR (80 : 20), exhibiting a broad particle-size distribution, that is, there are particles with a size ranging from approximately 2 to 10 μm. Almost all the EOR particles are pulled out of the matrix during cryofractioning, that is, the elastomer particles are removed due to the lack of adhesion between EOR and SMA. The reactive system SMA/EOR-*g*-OXA (80 : 20) [Fig. 4(b)] exhibits a much finer morphology with particles smaller than 0.5 μm.

Figure 4(c,d) shows the fracture surfaces of the nonreactive and reactive blend with the composition ratio 20 : 80. In the SMA/EOR blend (20 : 80), particles ranging from approximately 0.5 to 3 μm are present, whereas in the reactive system SMA/EOR-*g*-OXA, no particles >0.2 μm can be observed. It can be seen that the brittle SMA particles are partially broken during fracture. At both blend ratios, the size of the dispersed phase is significantly decreased in the case of the reactive, that is, the oxazoline-modified system with respect to that of the nonreactive system. Another interesting feature can be noticed when comparing the two blend ratios, that is, 80 : 20 and 20 : 80. At the blend ratio of 80 : 20, the particles are always larger than those of the blend with a composition ratio 20 : 80. This is due to the viscosity ratio of SMA and EOR, where the zero shear viscosity (η_0) of EOR is larger than the η_0 of SMA.

The dynamic storage modulus, E', and tan(δ) values of the blends are shown in Figure 5. The nonreactive system SMA/EOR (75 : 25) is represented by open symbols and the reactive system SMA/EOR-*g*-OXA (75 : 25) is symbolized by filled symbols. The maximum of tan(δ), assigned to the glass transition temperature, is shifted from −49.5°C of the nonreactive system to −53.6°C of the reactive system. The T_g shift toward lower temperatures of the rubber phase was also observed in ABS[52,53] and attributed to increased dilatation of the rubber phase due to thermal stress. The storage moduli, E', for $T > T_g$ (EOR)

Figure 4 Morphology of SMA/EOR melt blends obtained by ESEM (T = 225°C, 90 rpm, t = 7 min): (a) SMA/EOR (80 : 20); (b) *in situ* compatibilized SMA/EOR-*g*-OXA (80 : 20); (c) SMA/EOR (20 : 80); (d) *in situ* compatibilized SMA/EOR-*g*-OXA (20 : 80).

are significantly higher for the reactive system. The explanation for the increased moduli is not trivial as the blends under investigation exhibit a significant different particle-size distribution for the dispersed phase. Besides this difference in morphology, interfacial effects in the reactive system, that is, crosslinking at the interface, might be responsible for this behavior.

Figure 5 DMA traces of SMA blends containing 25 wt % EOR and EOR-*g*-OXA, respectively. Open symbols represent SMA/EOR; full symbols depict the reactive system SMA/EOR-*g*-OXA.

It was shown that reactive processing of SMA with EOR-*g*-OXA provides a reduction of the particle size of the dispersed phase. In addition, a shift of the glass transition toward lower temperature with respect to the nonreactive system is observed, indicating strong bonding between the phases.

Reactive Blending of the Ternary Blend SAN/SMA/EOR-*g*-OXA

Pure SAN was blended with EOR and with EOR-*g*-OXA with an elastomer weight fraction ranging from 0 to 25 wt % without any compatibilizer. To study the influence of a reactive compatibilizer, the SMA weight fraction, X, was varied. In Figure 6, the torque values of SAN/SMA/EOR-*g*-OXA blends (80-X : X : 20) are depicted. The addition of small amounts of SMA (X = 2–8) accounts for a large increase of torque when compared to the torque of the nonreactive system. Further addition of SMA does not lead to a significant further increase of torque, even at X = 80, which is equivalent to a complete exchange of SAN by SMA in the blend. This indicates that already small amounts of SMA are sufficient for effective reactive compatibilization.

Figure 6 Torque–time relationship for SAN/SMA/EOR-*g*-OXA blends (80-*X*: *X*:20) (*T* = 225°C, 90 rpm, *t* = 7 min). SAN is replaced by increasing amounts of the reactive compatibilizer SMA, X: X = 0 (0%); 2 (2.5%); 4 (5%); 8 (10%); 16 (20%); 80 (100%).

Mechanical Properties

Table II depicts the mechanical properties of the prepared blends. As expected, the Young's modulus and tensile strength of the SAN/EOR blends decrease significantly with increasing amounts of

EOR. However, elongation at break and the impact properties remain unchanged. To examine the capability of SMA to act as a reactive compatibilizer for SAN/EOR-*g*-OXA blends, compositions 80 : 20 and 75 : 25 were studied in detail. For these compositions, different amounts of SAN are replaced by SMA (0, 2.5, 5, 10, 20, and 100%). The Young's modulus and tensile strength of these ternary blends are almost independent of the added amount of SMA. However, the binary blends without any SAN, that is, SMA/EOR blends, show a reduced tensile strength, which is explained in terms of the poor mechanical properties of neat SMA.

The notched Izod impact strength of the blends under investigation is shown in Figure 7. Increasing amounts of SMA lead to improved toughness of the ternary SAN/SMA/EOR-*g*-OXA blends. However, the maximum impact strength is achieved for binary SMA/EOR-*g*-OXA blends, that is, blends without any SAN. The analogous nonreactive SMA/EOR blends exhibit brittle behavior, whereas the tensile properties are in the same order of magnitude. Thus, reactive processing of EOR-*g*-OXA leads to improved impact properties (up to 10.7 kJ/sqm in binary SMA blends).

Table II Mechanical Properties of SAN/SMA Blends with EOR and EOR-*g*-OXA

SAN (wt %)	SMA (X) (wt %)	EOR (wt %)	EOR-*g*-OXA (wt %)	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Notched Izod Impact Strength (kJ/sqm)
100	—	—	—	3700	72	5.2	1.4
90	—	10	—	3017	44	5.8	1.5
80	—	20	—	2477	35	5.9	1.4
75	—	25	—	1917	26	5.1	1.4
70	—	30	—	1634	23	5.3	1.5
80	—	—	20	2310	26	4.5	1.3
78	2 (2.5%)[a]	—	20	2120	26	5.8	1.6
76	4 (5%)[a]	—	20	2130	25	8.3	2.0
72	8 (10%)[a]	—	20	2285	28	6.4	2.4
64	16 (20%)[a]	—	20	2263	27	4.3	3.6
—	80 (100%)[a]	—	20	2166	25	<1	4.8
—	80	20	—	2112	25	<1	1.0
75	—	—	25	1952	28	5.0	1.4
73.38	1.62 (2.5%)[a]	—	25	1944	28	5.5	1.5
71.75	3.25 (5%)[a]	—	25	1960	28	9.1	1.7
67.5	7.5 (10%)[a]	—	25	1921	25	10.1	3.4
60	15 (20%)[a]	—	25	1984	29	11.7	5.8
—	75 (100%)[a]	—	25	1893	17	<1	10.7
—	75	25	—	1948	17	<1	1.0

[a] % SAN replaced by SMA [= SMA/(SAN + SMA)].

Figure 7 Notched Izod impact strength of SAN/SMA/EOR-*g*-OXA melt blends with two different blend ratios (different amounts of SAN are replaced by SMA).

Blends containing 25 wt % of rubber exhibit better impact properties compared to blends with a 20 wt % rubber fraction. In ternary blends, elongation at break increases with increasing substitution of SAN by SMA. However, the binary blends without any SAN, that is, SMA/EOR blends, show a small elongation at break. The improved toughness in SAN/EOR-*g*-OXA blends containing SMA clearly indicates that SMA is able to act as a reactive compatibilizer.

Morphology Study

Figure 8 depicts the morphology of the cryofractured samples of SAN/SMA/EOR-*g*-OXA (80-*X* : *X* : 20) melt blends with increasing amounts of SMA obtained by ESEM. Figure 8(a) shows SAN/EOR-*g*-OXA at a blend composition 80 : 20. The dispersed phase consists of large particles. More than 50% of the particles are pulled out of the matrix, thus indicating poor adhesion between SAN and EOR-*g*-OXA. Figure 8(b) shows the analogous system containing 2.5% SMA. The rubber particles are not pulled out of the matrix; instead, fracture proceeds through the rubber particles. This provides good evidence for the location of SMA at the SAN/EOR-*g*-OXA interface, even at a low concentration of SMA. Already, small amounts of SMA give improved adhesion at the SAN/EOR interface. SMA was selected with a low amount of MA in order to afford miscibility with SAN and a small interfacial tension with EOR. In Figure 8(c), the matrix contains 5% of SMA. The particle size of the dispersed phase is decreased significantly, with the average particle

Figure 8 Morphology of SAN/SMA/EOR-*g*-OXA (80-*X* : *X* : 20) melt blends with increasing amounts of SMA obtained by ESEM: *X* = (a) 0 (0%), (b) 2 (2.5%), (c) 4 (5%), (d) 8 (10%), (e) 16 (20%), and (f) 80 (100%).

Figure 8 (*Continued from the previous page*)

size found to be in the range of 400–500 nm. At least 5% of the reactive compatibilizer is needed to achieve particle-size reduction of the dispersed phase. Figure 8(d) depicts the blend containing 10% of SMA. The average particle size is even smaller. Figure 8(e) shows the blend with 20% SMA, exhibiting the same morphology as that of the system with 10% SMA. In conclusion, 5–10% of the reactive compatibilizer is necessary to achieve an optimum reaction between the rubber and the matrix. Figure 8(f) shows the pure SMA/EOR-*g*-OXA blend. The particle diameter of the rubber is very similar to that shown in Figure 8(e). Improved impact strength is always accompanied by a pronounced particle-size reduction of the dispersed rubber phase. A small particle size combined with good interfacial adhesion is a prime requirement for enhanced toughness.

To study the morphology of the matrix/rubber interface, the nonreactive and the reactive system containing 25 wt % of EOR was investigated us-ing TEM. The particle size of the nonreactive, that is, uncompatibilized, blends are in the range 10–50 μm. Furthermore, bad adhesion between the two phases is detected. This behavior can also be observed during cryosectioning when preparing ultrathin sections for TEM. The rubber particles are pulled out during sectioning. Thus, in TEM, only holes or deformed particles are observed. Therefore, no TEM micrograph of this system is depicted here. However, entirely different features are observed for the system SAN/SMA/EOR-*g*-OXA 60/15/25. Figure 9 shows TEM micrographs of SAN/SMA/EOR-*g*-OXA (60 : 15 : 25) (process temperature of 225°C, 90 rpm, t = 7 min). The particle size of the rubber phase is in the range 300–400 nm. The elastomer particles are not spherical but they are deformed. The particles appear fairly well stabilized by *in situ* encapsulation of the EOR with a SMA shell. The shell, derived from SMA-*g*-EOR, reduces the interfacial tension between SAN and EOR. Further-

Figure 9 TEM micrographs of SAN/SMA/EOR-*g*-OXA (60 : 15 : 25) (T = 225°C, 90 rpm, t = 7 min).

Figure 10 Mean particle size of SAN/EOR (75 : 25) and SAN/SMA/EOR-*g*-OXA (60 : 15 : 25) (T = 225°C, 90 rpm, accepted t = 7 min) after further annealing at different temperatures for different annealing times.

more, it can be observed that the encapsulated rubber particles are accumulated into clusters.

To study the stability of the blend morphology, two systems (SAN/SMA/EOR-*g*-OXA 60 : 15 : 25 and SAN/EOR 75 : 25) were annealed for different time periods. The mean particle size of the dispersed rubber phase was determined using TEM. The mean particle size of the uncompatibilized system SAN/EOR 75 : 25 increases with increasing annealing time (Fig. 10). Also, the dispersed particle size increases with annealing temperature. The reactive system does not show any significant increase of the mean particle size, that is, coalescence upon isothermal annealing. Coalescence can be observed in immiscible blends with high interfacial tension and is thermodynamically driven by minimizing the interfacial area of the blend components.[54–56] The SMA forms an interphase around the rubber particles, leading to the steric hindrance and thus suppression of coalescence.

CONCLUSIONS

It has been shown that metallocene-based EOR can successfully be functionalized by melt free-radical grafting of OXA-MAL to serve as a compatibilizer. Oxazoline-functionalized EOR reacts with the MA groups of SMA during reactive processing, although the reaction products are not identified. The particle size of the respective dispersed phase is lowered significantly. Furthermore, a significant decrease of the glass transition temperature of the dispersed rubber phase can be

observed, indicating good adhesion between the matrix and rubber.

SMA is able to act as a reactive compatibilizer in SAN/EOR-*g*-OXA blends. Small amounts of SMA are sufficient to achieve a finer dispersion of the rubber phase. Further addition leaves the morphology unchanged, but impact properties are significantly improved upon addition up to 20% of SMA with the stiffness kept. The ternary, that is, reactive, modified system exhibits an interphase of SMA, covalently bonded to EOR-*g*-OXA and physically linked to SAN. The morphology is stable against coalescence during 24-h annealing at 280°C. SAN blends with EOR do not contain double bonds and are expected to exhibit much better weatherability with respect to ABS.

Other MA-containing copolymers could be used as reactive compatibilizers in combination with oxazolines. A wide range of oxazoline-functionalized rubbers, such as oxazoline-functionalized nitrile rubbers,[57–60] are available for reactive processing in the presence of anhydride-functional thermoplast.

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