

Compatibility Study of Natural Rubber and Ethylene–Propylene–Diene Rubber Blends

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ABSTRACT: The compatibility of natural rubber/ethylene–propylene–diene monomer (EPDM) blends with and without different compatibilizers was evaluated with viscosity measurements, differential scanning calorimetry, and scanning electron microscopy. The blends were modified with two methods. In the first method, high-energy radiation, in the form of γ -rays, was used to create crosslinks (chemical bonds) between the rubber chains at the domain boundaries. In the second method, various compatibilizers, such as ethylene–propylene–diene monomer-*g*-maleic anhy-

dride (prepared by the radiation-induced graft copolymerization of EPDM with maleic anhydride), polybutadiene rubber, chlorinated rubber, chlorosulfonated polyethylene, and poly(vinyl chloride), were used. The results revealed that the addition of a small percentage of a compatibilizer reduced the domain size of the dispersed phase. Furthermore, the compatibility and properties of the blends were greatly enhanced and improved. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1–11, 2003

INTRODUCTION

The blending of two or more rubber types is a useful technique for the preparation of materials with properties absent in the component rubbers.^{1–4} Natural rubber (NR) and its blend compounds have extensively been studied because of their superior performance in tire applications. The incorporation of a suitable amount of ethylene–propylene–diene monomer (EPDM) into a diene rubber provides a significant improvement in heat and ozone resistance.^{5–7}

Polymer blends generally exhibit poor mechanical properties because of incompatibility and phase separation.^{8–11} Several attempts have been made to minimize phase separation and increase interfacial adhesion. These include the addition of a compatibilizing agent such as a third polymer, that is, a graft or block copolymer that improves the interactions between constituent polymers.^{12–17} Interfacial agents, including both reactive and nonreactive types, for polymer blends and composites have been the subjects of some reviews.^{17–19} The compatibilization of polymer blends through reactions during compounding is becoming increasingly important. Consequently, compatibility is a fundamental property in polymer blends, deciding their practical utility. The degree of compatibility has been studied theoretically and experimentally with different methods, such as viscosity measurements,¹⁷

ultrasonic techniques,²⁰ heat-of-mixing measurements,²¹ differential scanning calorimetry (DSC), and dynamic mechanical spectroscopy.²²

The aim of this study was to improve the compatibility of NR/EPDM blends either by the introduction of a third polymer, such as polybutadiene rubber (BR), chlorinated rubber, chlorosulfonated PE, or poly(vinyl chloride) (PVC), or by exposure to γ -radiation for the purpose of creating crosslinks between the rubber chains or producing ethylene–propylene–diene monomer-*graft*-maleic anhydride (EPDM-*g*-MAH), which could act as a compatibilizer.

EXPERIMENTAL

Materials

NR (ribbed smoked sheets; RSS-1) was supplied by the Transport and Engineering Co. (Alexandria, Egypt); it had a specific gravity of 0.913 ± 0.005 and a Mooney viscosity [$M_L(1+4)$] at 100°C of 60–90. EPDM (Vistalon 6505) was produced by ESSO Chemi Germany; the diene (ethylidene norbornene) content was 9%, the ethylene content was 55%, $M_L(1+8)$ at 127°C was 48–52, and the density was 0.86.

The compatibilizers were BR (97% 1,4-*cis* form, specific gravity = 0.915 ± 0.005 , $M_L(1+4)$ at 100°C = 35 ± 3), PVC (suspension polymer, $K = 68$), chlorinated rubber ($C_{10}H_{11}Cl_{17}$, yellowish powder, specific gravity = 1.63–1.66), chlorosulfonated polyethylene (PE; white chips, specific gravity = 1.12, sulfur content = 1.4%, chlorine content = 26%), and maleic acid anhydride (mp = 52.5°C, bp = 202°C, specific gravity = 1.48).

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Blend preparation

The graft polymer EPDM-g-MAH was prepared with EPDM rubber as a backbone polymeric chain and maleic anhydride (MAH); γ -radiation was used as a polymerization initiator.

The components were masticated on a two-roll mill for 5 min, and then each blend was mixed in a Brabender plasticorder at a rotor speed of 70 rpm. The mixing temperature was 150°C. The mixing was continued for 5 min for the compatibilized systems.

The amount of each compatibilizer (BR, chlorinated rubber, chlorosulfonated PE, and PVC) used was 10 parts. The compatibilizer was added to the blend composition, and the mixing was continued for another 5 min.

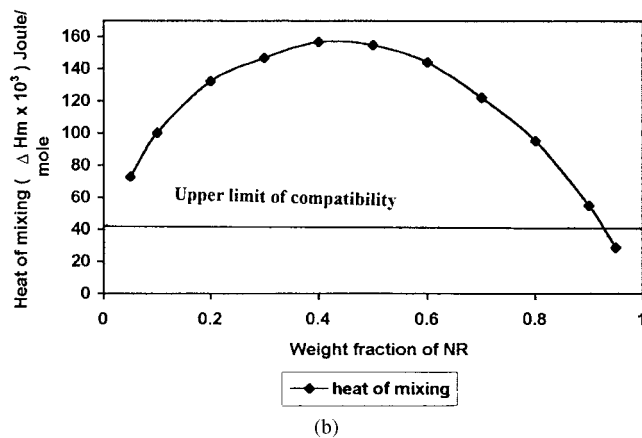
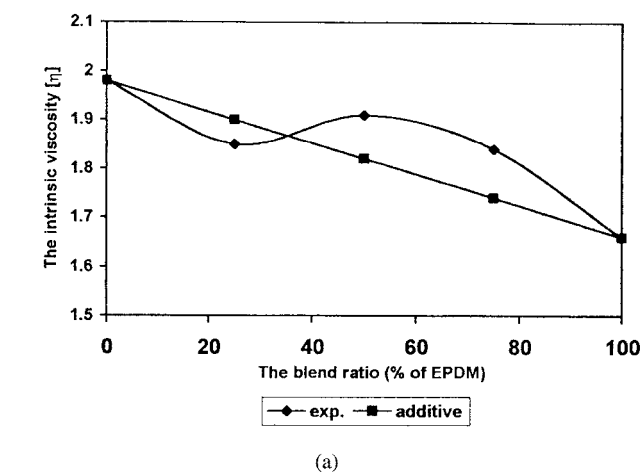


Figure 1 (a) Variation of $[\eta]$ with the blend ratio of NR to EPDM [(\blacklozenge) experimental data and (\blacksquare) additive] and (b) heat of mixing as a function of the composition in a blend of NR and EPDM [(\blacklozenge) heat of mixing].

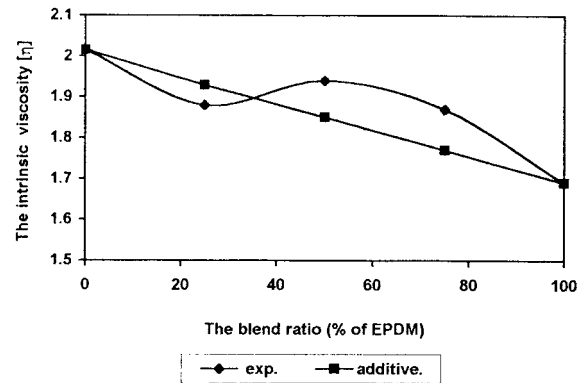


Figure 2 Variation of $[\eta]$ with the blend ratio of NR to EPDM after 2 k gray of irradiation [(\blacklozenge) experimental data and (\blacksquare) additive].

Measurements

The viscosity measurements were carried out with a modified Ostwald dilution viscometer.¹⁷

IR spectroscopy and DSC were carried out at the Microanalytical Center at Cairo University. The IR spectra were recorded on a Bruker Vector 22 spectrophotometer (Germany) with KBr. DSC was performed with a Shimadzu DSC-50.

Scanning electron microscopy (SEM) was used to study the characteristics of the fracture surfaces of the grafted NR/EPDM blends. SEM micrographs of the surfaces of rubber specimens were created with a JSM-T20 electron microscope (JEOL, Japan). For SEM observations, the polymer was mounted on a standard specimen stub; a thin coating ($\sim 10^{-8}$ m) of gold was deposited onto the polymer surface and attached to the stub before the SEM examination to enhance the conductivity and secondary electron emission characteristics of the overgrowth.

The irradiation of the rubber samples was carried out at the Middle East Regional Radioisotope Center for Arab Countries. A 4000 γ -chamber, providing a

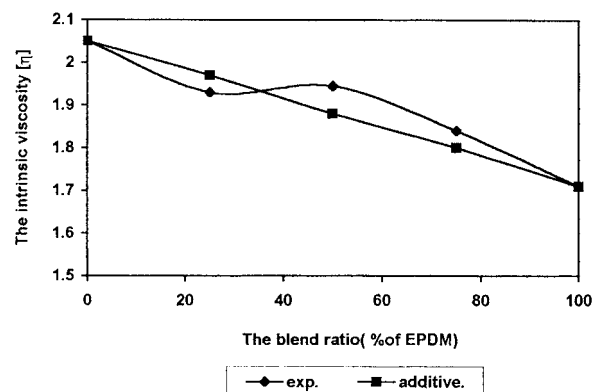


Figure 3 Variation of $[\eta]$ with the blend ratio of NR to EPDM after 4 k gray of irradiation [(\blacklozenge) experimental data and (\blacksquare) additive].

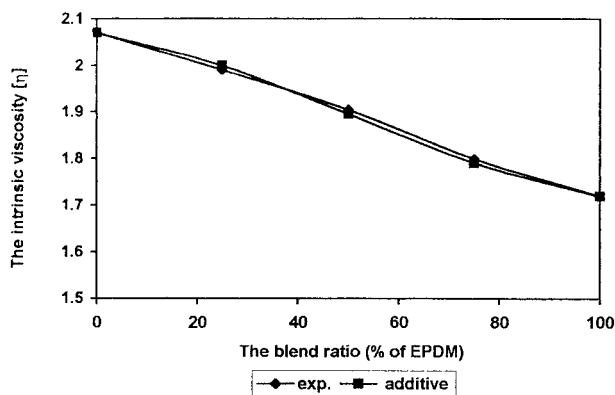


Figure 4 Variation of $[\eta]$ with the blend ratio of NR to EPDM after 6 k gray of irradiation [(♦) experimental data and (■) additive].

type of atomic energy, was used to give a dose rate of about 96 rad/s. The irradiation temperature was about 40°C.

RESULTS AND DISCUSSION

The viscosity measurements were used as the principal means of examining the compatibility of the NR/EPDM rubber blends;²³ it was interesting to study the rheological behavior of rubber blends in solutions to establish the general shape of the viscosity–composition curves for the blends under investigation. The degree of compatibility of NR with EPDM was determined according to the linearity behavior of the curves.

The specific viscosity (η_{sp}) for different concentrations (C) was measured, and when η_{sp}/C was plotted against C , straight lines were obtained. Their intersections with the η_{sp}/C axis represented the intrinsic viscosity ($[\eta]$) of the NR/EPDM blends.

The changes in $[\eta]$ with the NR/EPDM blend compositions are shown in Figure 1(a). The straight line represents the additive values of $[\eta]$ at different compositions, whereas the experimental data are shown by an S-shape curve, which deviates from the additivity line. The observed nonlinear behavior indicates the multiphase nature of this blend.^{16,17}

Also, when the heat of mixing²¹ over the entire range of compositions and weight percentages for NR/EPDM was calculated, it was found to lie in the range of 28.7×10^{-3} to 72.7×10^{-3} J/mol, and these values were above the limiting value of compatibility. This result implies that macromolecules in this mixture were in a disordered state, and so this blend system could be considered a thermodynamically incompatible blend [Fig. 1(b)].

The heterogeneity of the NR/EPDM blend system was emphasized by the differences in the solubility parameters of the two rubbers. This was calculated

theoretically from the heat of mixing with the Schneier equation²¹ because the solubility parameter for NR was known [$\delta = 8.35$ (cal/cc)^{1/2}];²⁴ however, the solubility parameter of EPDM was not known. It was calculated according to Krause and coworkers:^{13,25} $\delta = \sum \delta_i \phi_i$, where ϕ_i is the volume fraction of each component from Small's equation,¹³ $\delta = \rho \sum F_i / M$, where ρ is the density of the polymer at the temperature of interest, M is the molecular weight of the repeat unit in the polymer, and $\sum F_i$ is the sum of the molar attraction constants of all the chemical groups in the polymer repeat unit. Therefore, δ for EPDM was 7.74 (cal/cc)^{1/2}. Barlow and Paul¹⁰ showed that closely matching solubility parameters ($\delta_1 - \delta_2 = 0.1$) would result in the complete miscibility of two polymers as long as their molecular weight exceeded 30,000; the wide gap of the solubility parameters (0.61) between NR and EPDM predicted incompatibility.

To overcome the problem of phase separation in NR/EPDM blends, we made trials with different compatibilizers. That is, the compatibility of NR/EPDM blends could be improved either by the addition of a third component (compatibilizer) such as BR, chloro-sulfonated PE, PVC,^{15,16} or EPDM-g-MAH or by the creation of some crosslinks between the components of the blend by γ -irradiation.

Compatibilization via γ -irradiation

NR/EPDM blends of different ratios were irradiated with different doses of γ -rays (2, 4, 6, and 8 k gray).

The compatibility of the blends was evaluated by viscosity measurements. Figures 2–5 show the relationship between $[\eta]$ and the blend ratio. The radiation doses of 6 and 8 k gray were the most suitable for creating the crosslinks necessary for the mixing homogeneity of NR and EPDM, as shown by the good straight lines between $[\eta]$ and the blend ratios, which proved the compatibility of this investigated blend system at these radiation doses.

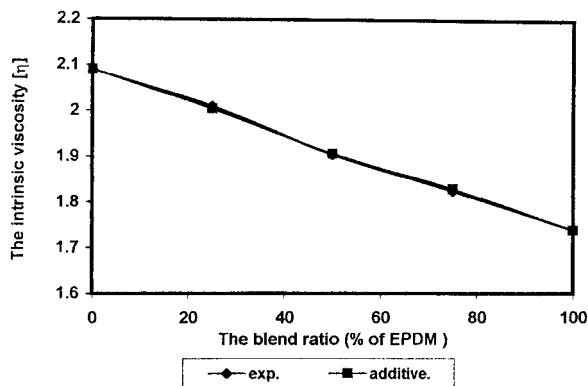
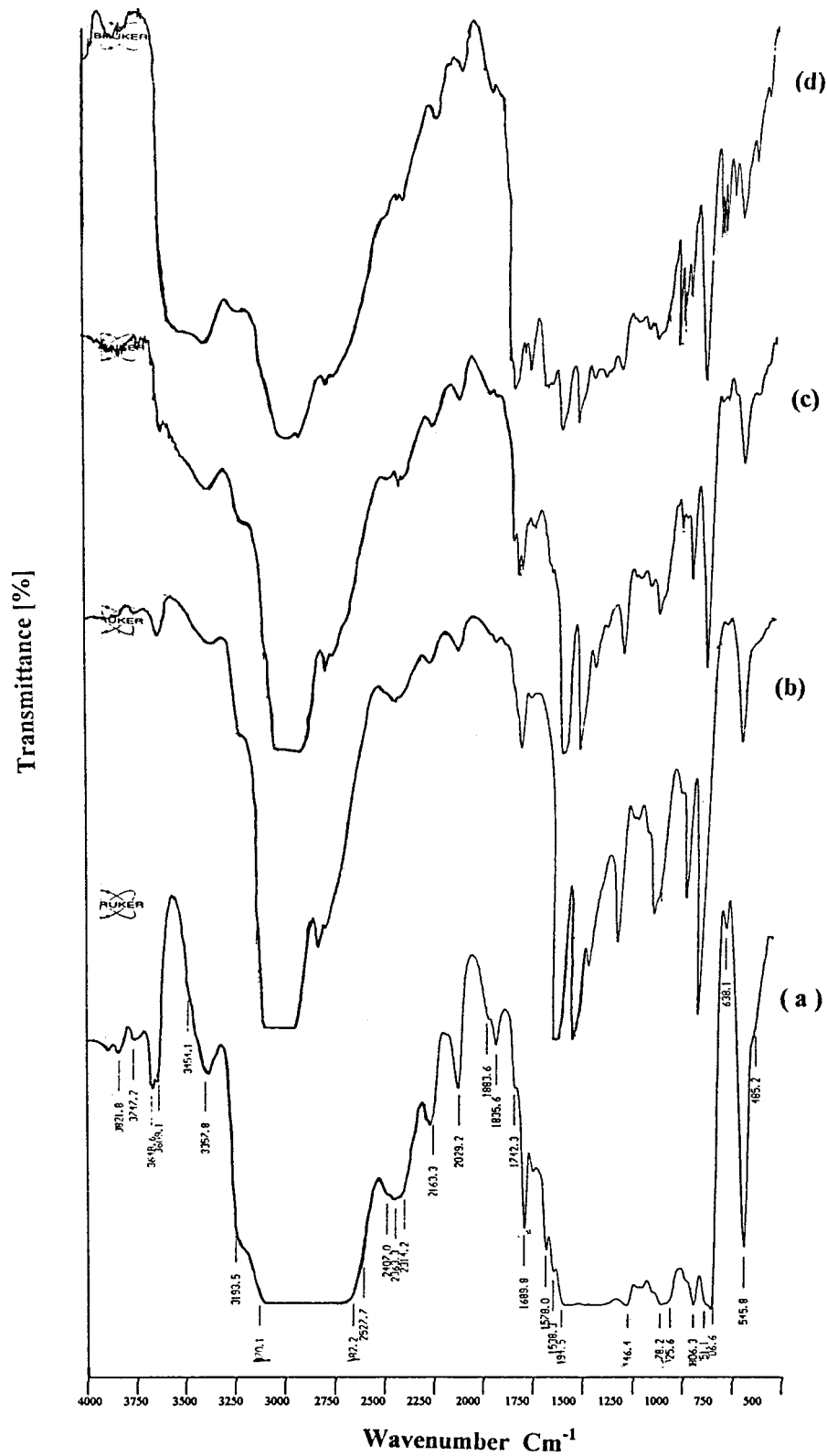


Figure 5 Variation of $[\eta]$ with the blend ratio of NR to EPDM after 8 k gray of irradiation [(♦) experimental data and (■) additive].



(a)

Figure 6 (A) IR spectra for (a) EPDM, (b) EPDM grafted with MAH (0.05% concentration) at 2 k gray, (c) EPDM grafted with MAH (0.07% concentration) at 2 k gray, and (d) EPDM grafted with MAH (0.1% concentration) at 2 k gray and (B) IR spectra for (a) EPDM, (e) EPDM grafted with MAH (0.05% concentration) at 4 k gray, and (f) EPDM grafted with MAH (0.07% concentration) at 4 k gray.

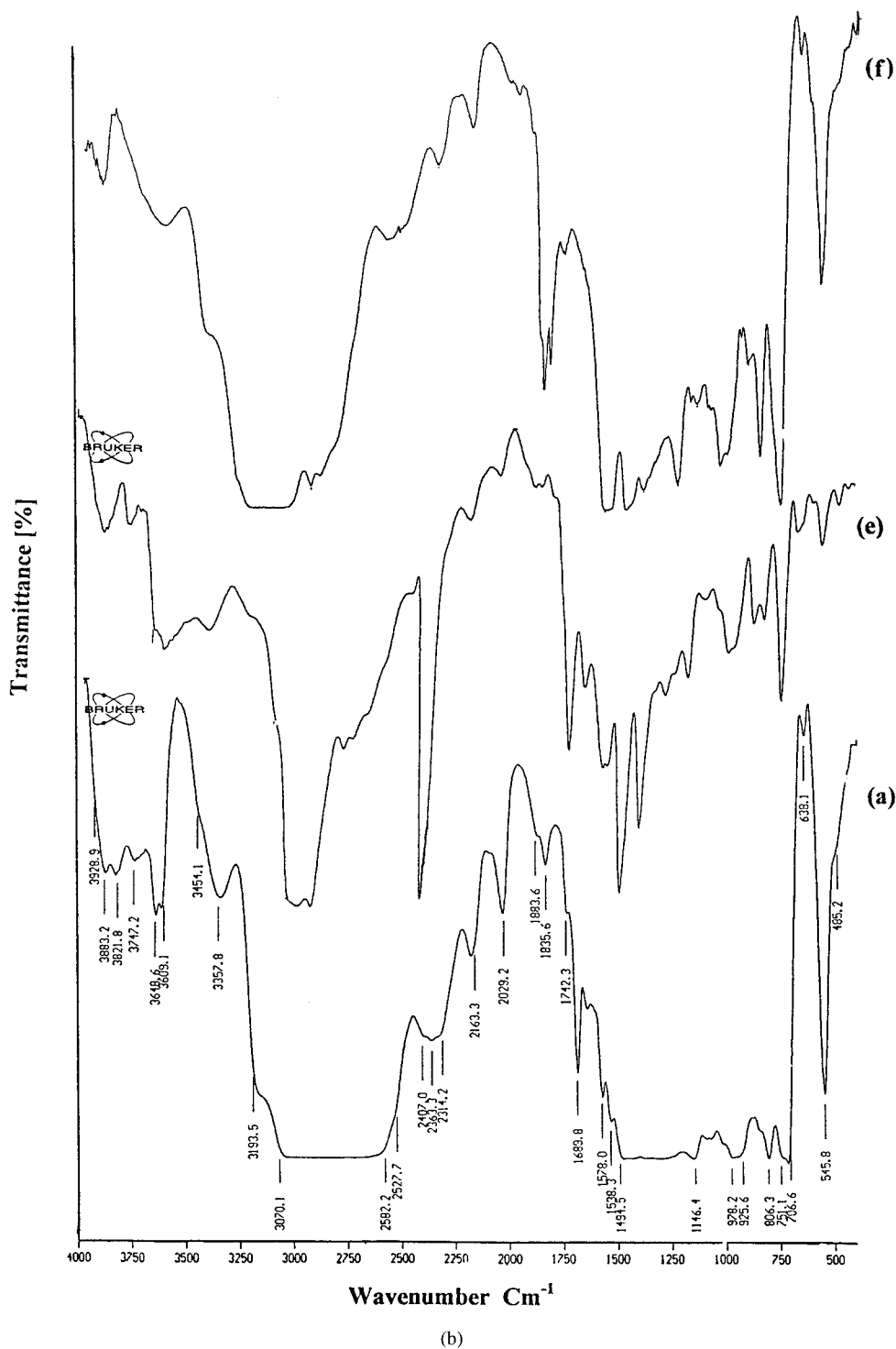


Figure 6 (Continued from the previous page)

Compatibilization with the EPDM-g-MAH copolymer

EPDM was grafted with different concentrations of MAH (0.05, 0.07, 0.1, and 0.2) under the action of γ -irradiation. The IR spectra of EPDM grafted with MAH are shown in Figure 6.

For EPDM-g-MAH, four strong absorption bands at 1740, 1638.5, 1155.6, and 722 cm^{-1} were observed due

to the stretching absorption of C=O, C=C, —C—O, and CH bending frequencies of MAH; this confirmed that grafting by MAH occurred on the EPDM chains. The optimum grafting yield was 14%, as shown in Table I, at 4 k gray and at an MAH concentration of 0.07%.

The concentration of the compatibilizer was selected to be 10%, which was found to be very suitable. Figure

TABLE I
Graft yield of EPDM Grafted by MAH

Radiation dose (k gray)	Concentration of MAH (%)	Graft yield (%)
2	0.05	5.4
2	0.07	7.26
2	0.1	6.1
2	0.2	Gel
4	0.05	8
4	0.07	14
4	0.1	Gel
4	0.2	Gel
6	0.05	Gel
6	0.07	Gel
6	0.1	Gel
6	0.2	Gel

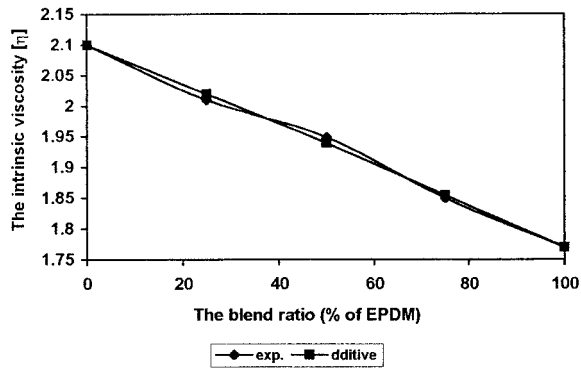


Figure 7 Variation of $[\eta]$ with the blend ratio of NR to EPDM with 10 phr EPDM-g-MAH [(♦) experimental data and (■) additive].

7 shows the linear relationship of $[\eta]$ with the blend composition of NR/EPDM compatibilized with 10% EPDM-g-MAH. This confirms the complete homogeneity of these two rubbers in each other. In other words, the graft polymer could act as an effective compatibilizer for the NR/EPDM blend.

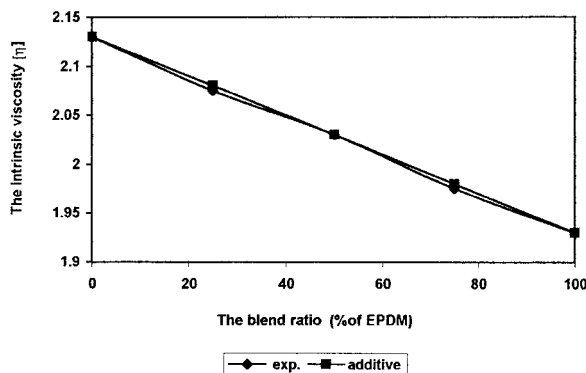


Figure 8 Variation of $[\eta]$ with the blend ratio of NR to EPDM with 10 phr chlorinated rubber [(♦) experimental data and (■) additive].

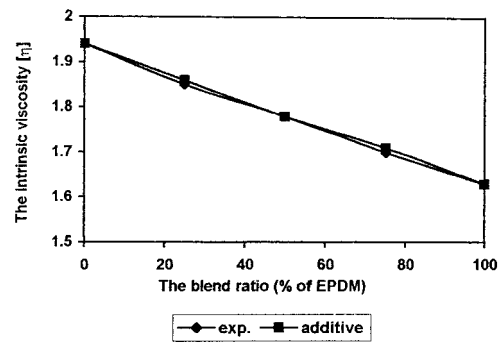


Figure 9 Variation of $[\eta]$ with the blend ratio of NR to EPDM with 10 phr BR [(♦) experimental data and (■) additive].

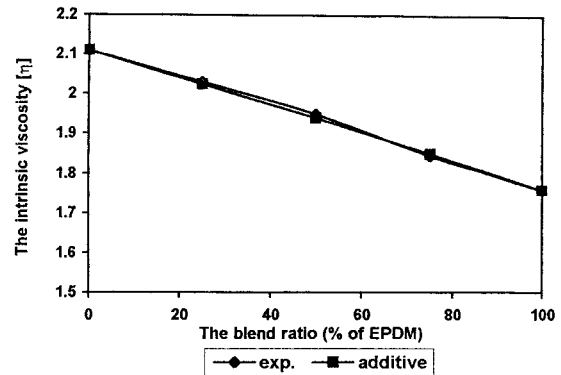


Figure 10 Variation of $[\eta]$ with the blend ratio of NR to EPDM with 10 phr chlorosulfonated PE [(♦) experimental data and (■) additive].

Effects of some other compatibilizers

Some other compatibilizers, such as chlorinated rubber, BR, chlorosulfonated PE, and PVC, with an optimum concentration of 10 phr were investigated by a viscometric technique, and the results are illustrated

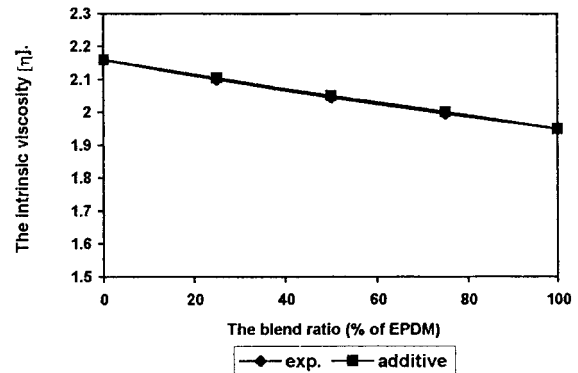
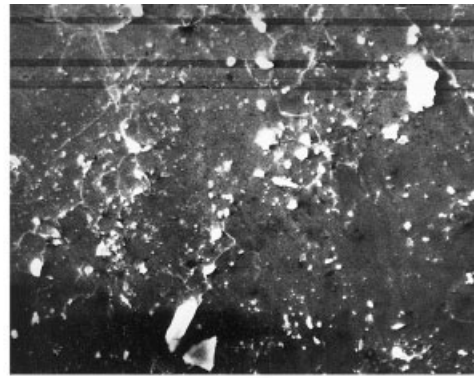


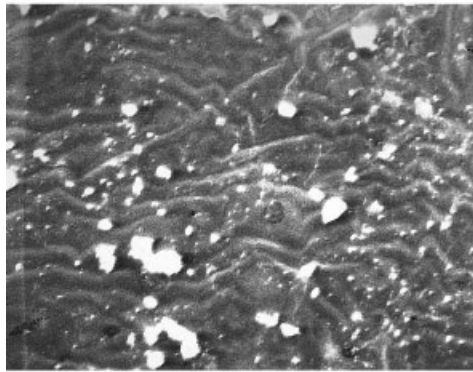
Figure 11 Variation of $[\eta]$ with the blend ratio of NR to EPDM with 10 phr PVC [(♦) experimental data and (■) additive].



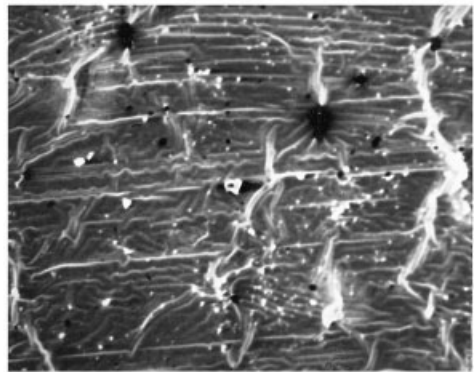
(a)



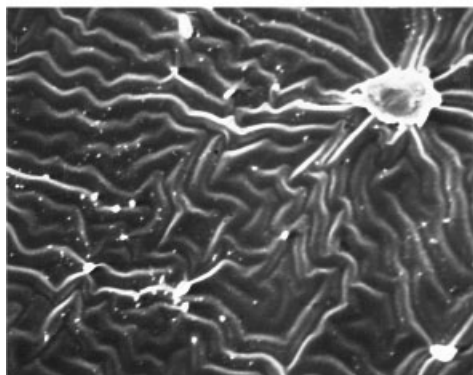
(b)



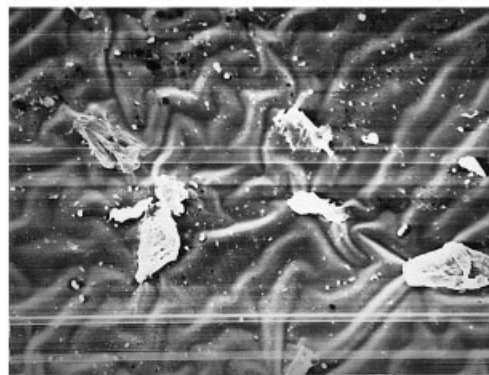
(c)



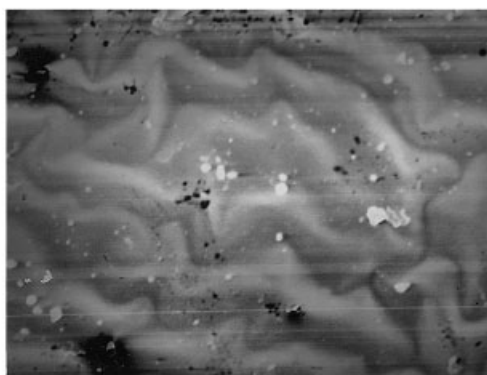
(d)



(e)



(f)



(g)

Figure 12 SEM micrographs (original magnification, 1000 \times): (a) 50/50 NR/EPDM without a compatibilizer, (b) NR/BR/EPDM, (c) NR/PVC/EPDM, (d) NR/chlorinated rubber/EPDM, (e) NR/chlorosulfonated PE/EPDM, (f) NR/ γ -radiation/EPDM, and (g) NR/MAH/EPDM.

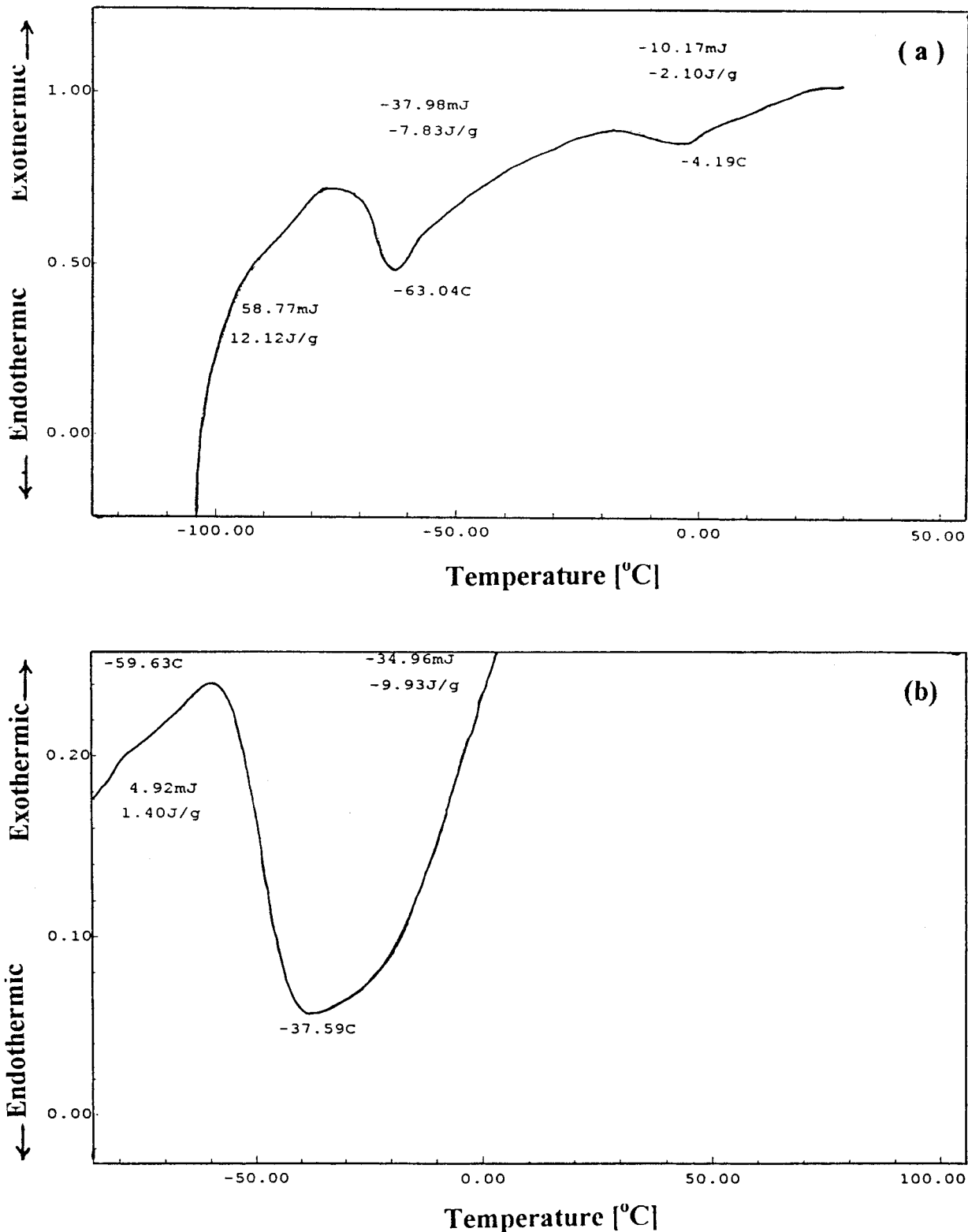


Figure 13 DSC spectra of (a) NR, (b) EPDM, (c) 50/50 NR/EPDM, (d) NR/BR/EPDM, (e) NR/PVC/EPDM, (f) NR/MAH/EPDM, (g) NR/ γ -radiation/EPDM, (h) NR/chlorinated rubber/EPDM, and (m) NR/chlorosulfonated PE/EPDM.

in Figures 8–11. The linearity in these figures confirms the great improvement in the homogeneity of the NR/EPDM blend in the presence of these compatibilizers.

Electron microscopy investigations

The electron micrograph in Figure 12(a) shows the morphology of a 50/50 (w/w) NR/EPDM blend. An

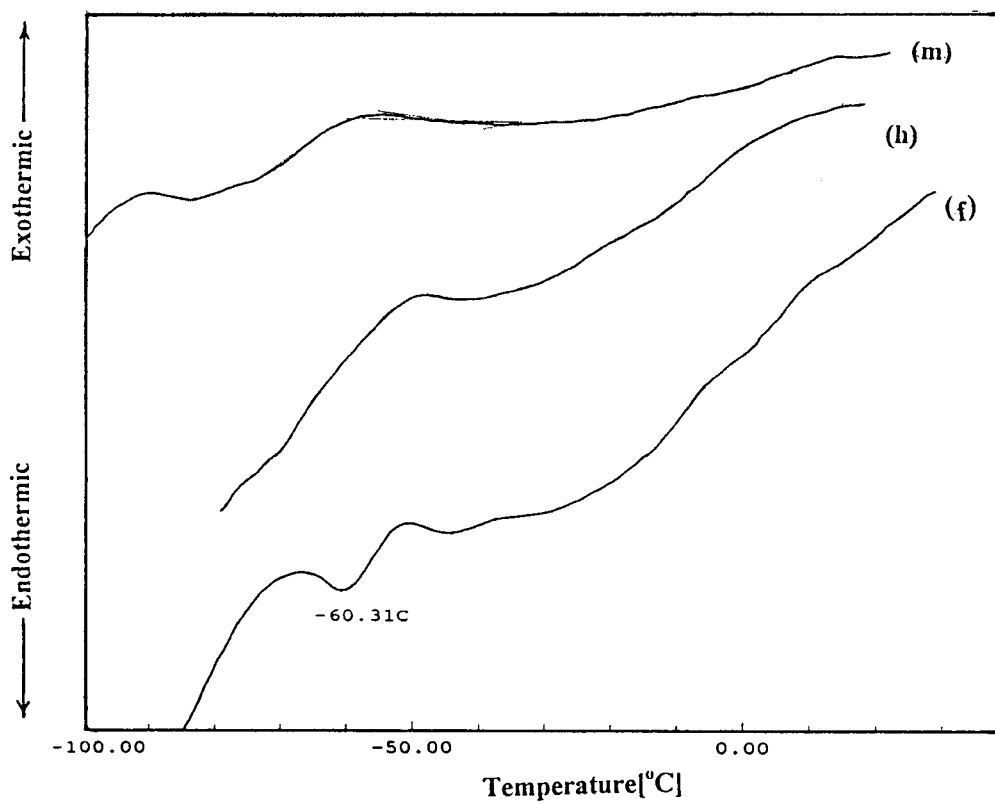
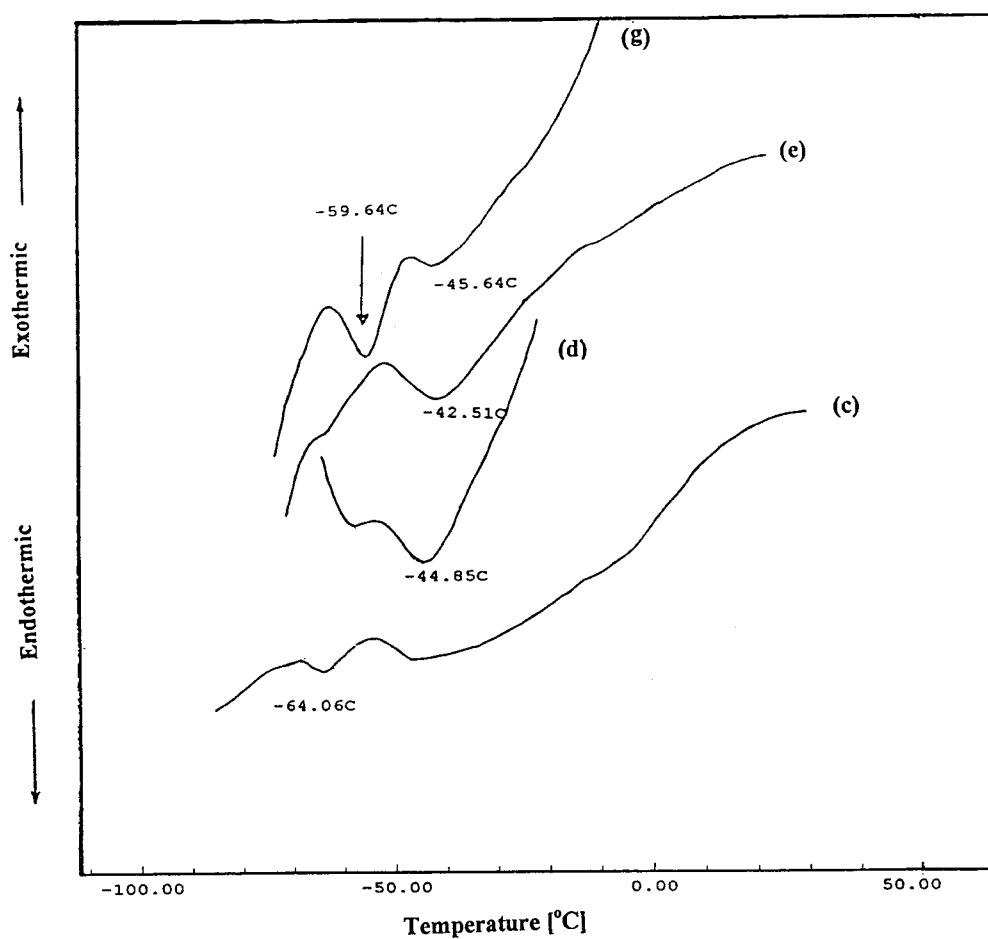


Figure 13 (Continued from the previous page)

TABLE II
DSC Results Obtained for NR, EPDM, and 50/50 NR/EPDM Without and with Compatibilizers

Sample code	Contribution from NR		Contribution from EPDM	
	T_g (°C)	Shift in NR T_g (°C)	T_g (°C)	Shift in EPDM T_g (°C)
NR	-63	—	—	—
EPDM	—	—	-37	—
NR/EPDM (without compatibilizer, control)	-64	—	-45	—
NR/BR/EPDM	-58	6	-44	1
NR/PVC/EPDM	-62	2	2.5	2.5
NR _g MAH/EPDM	-60	4	-40	5
NR/ γ -radiation/EPDM	-59.6	4.4	-45.6	-0.6
NR/chlorinated rubber/EPDM (one glass transition)	-48	12	-48	-3
NR/chlorosulfonated PE/EPDM (one glass transition)	-60	4	-60	-14

inspection of this micrograph indicates two phases with irregular domain sizes and shapes. This means that the NR/EPDM blends were completely immiscible, large EPDM domains being dispersed in the NR matrix. The average domain size of the dispersed phase was 4.1 μm . The compatibility of the NR/EPDM system was improved by the addition of a compatibilizer, as can be seen in Figure 12(b–g); the treatment resulted in noticeable surface hardening, and the physical changes in the surface were expected to influence physically both the deformation and adhesion of the two rubbers. In other words, the compatibilizers improved both the morphology and compatibility of the blends because of the reduction in the interfacial tension between EPDM and NR rubbers. The size of the dispersed phase (EPDM) domain decreased with the addition of compatibilizers, and no gross phase separation was present in the blends. For NR/BR/EPDM, the domain size was approximately 3.8–1.26 μm , whereas the average domain size decreased in the other cases (NR/PVC/EPDM, 2.7–0.75 μm ; NR/chlorinated rubber/EPDM, 1.95–0.5 μm ; NR/chlorosulfonated PE/EPDM, 2–0.75 μm ; NR/ γ -radiation/EPDM, 4–1.5 μm ; and NR/MAH/EPDM, 1–0.25 μm).

Generally, the obtained results complied with the conclusions of Koberstein et al.,²⁶ Legge et al.,²⁷ and Meier,²⁸ who reported that compatibilizers reduced the phase domain size.

DSC

The thermal characteristics of NR, EPDM, and their blend (50/50 NR/EPDM) were examined with a DSC technique from -100 to $+50^\circ\text{C}$; this allowed the identification of the glass-transition temperatures (T_g 's) of NR, EPDM, and their blend. Table II lists the T_g values for NR, EPDM, and their blend with and without compatibilizers, and Figure 13 shows scan traces.

For the 50/50 (w/w) NR/EPDM blend, there were two distinct glass transitions; the lower glass

transition was due to the EPDM phase, and the higher glass transition was due to the NR phase. The large melting endotherm was attributable to the high crystallinity of EPDM. We should note that the specific heat capacity depended on the type of rubber, the compatibilizer, and the concentration of the blend. A careful inspection of Table II shows that the mean T_g value of pure NR was -63°C , and this changed to -64°C in the blend; the T_g value of pure EPDM was -37°C , and this changed to -45°C in the blend. This may be due to some interaction between NR and EPDM at the boundaries of their phases forming a third phase.²²

DSC thermographs show the compatibilizing effects of BR, PVC, EPDM-g-MAH, and γ -radiation on NR/EPDM [Fig. 13(d–g)]. For each component in the blend, T_g showed a higher shift than that observed in the following order: NR/BR/EPDM > NR/ γ -radiation/EPDM > NR/MAH/EPDM > NR/PVC/EPDM. Only one T_g was detected after the addition of chlorinated rubber or chlorosulfonated PE to NR/EPDM blends, and this indicated the improved compatibility or dominance of these phases, as shown in Figure 13(h,m). However, when the compatibilizers were added to the blends, the glass transition became less distinct, and this indicated improved compatibility.

CONCLUSIONS

The incorporation of compatibilizers into NR/EPDM blends greatly enhanced their compatibility and greatly improved the rheological properties of the rubber blends. However, the compatibilizers were able to create a well-dispersed bicontinuous phase that exhibited rheological properties very similar to those obtained for compatible blends with one glass transition.

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