

Reactive Processing of Rubber–Plastic Blends: Role of Chemical Compatibilizer

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SYNOPSIS

The present investigation was aimed at understanding the role of chemical compatibilizers like carboxy-terminated nitrile rubber, amine-terminated nitrile rubber, liquid carboxylated nitrile rubber, etc., in the reactive processing of a dynamically vulcanized 50 : 50 nylon/HNBR blend. The interfacial parameters for a bilayer specimen of nylon and rubber and structure parameters during the processing were determined. The interfacial thickness (λ) increased from 48 to 70–80 nm and the interfacial tension (γ_{α}) decreased from 0.240 to 0.209–0.198 mN/m, depending on the nature and concentration of the compatibilizer. There was, however, an optimum level of the compatibilizer beyond which the thickness did not change significantly. For the ionomeric compatibilizer, λ decreased after the optimum concentration. The increase in λ is ascribed to the formation of a graft copolymer of nylon and rubber and the compatibilization reactions. Structure parameters were dependent upon the sequence of mixing of the compatibilizer. If the compatibilizer and the cross-linker were added in the rubber and the mixture was then added to nylon, the mean radius of the dispersed particle was smaller over the range of mixing times. The compatibilizers also reduced the particle size at the early stage of mixing due to reduced interfacial tension. In general, the particle size decreased with mixing time, attained a minimum, and then increased. The volume fraction of the interface was also very large for compatibilized systems. The particles were larger, however, when the compatibilizer was first mixed in nylon. SEM studies indicated that the compatibilizer in the latter case was not acting as a surfactant.

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INTRODUCTION

Blending of polymers is an interesting way of producing new materials with tailored properties. Most of the polymers are, however, incompatible due to the differences in their thermodynamic and viscoelastic properties, leading to an unfavorable interaction between molecular segments and poor dispersion of the components during mixing. As a result, immiscible blends have quite often lower mechanical properties than those of their components and the phase morphology is strongly dependent on the processing conditions. Efforts to deter-

mine the interrelationship among processing, morphology, and physical and mechanical properties of polymer blends and alloys have continued to burgeon. One of the ways to enhance interaction between components is to use compatibilizers, either block or graft copolymers added separately or generated *in situ*.¹ These are thought to be concentrated at the interface and act as emulsifiers, reducing interfacial tension. Reactive compatibilization using a suitably functionalized blend constituent or reactive copolymers is another technique and has been recently reviewed.² The problem of reactive compatibilization is more complicated in the case of dynamically vulcanized rubber–plastic blends. In this new class of materials, the rubber is vulcanized during processing. The plastic acting as a continuous phase allows for melt processing of the blends, whereas the dispersed rubber phase is responsible

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for rubber elasticity and other elastomeric properties. As a result, the properties of the blend depend on the morphology.

Coran³ reported on a large number of dynamically vulcanized rubber-plastic blends. It was documented that compatibilization was required for grossly dissimilar components, for instance, for a blend of nitrile rubber (NBR) and polypropylene (PP), to reduce interfacial tension and enable stronger interaction between the phases. Maleic-modified PP in conjunction with amine-terminated NBR had a significant effect on the properties and morphology of NBR/PP blends. A dimethylol phenolic compound was also effective in technological compatibilization of the above mixture. Similarly, the tensile properties of natural rubber (NR)/polyethylene (PE) blends were significantly improved with the addition of maleic-modified PE and epoxidized NR.⁴

Thermoplastic elastomeric blends of poly(butylene terephthalate) and ethylene propylene diene rubber (EPDM) could be compatibilized by using an EPDM-containing reactive epoxy group.⁵ The morphology and impact properties of poly(styrene-co-maleic anhydride)/bromobutyl rubber blends were described as a function of interfacial modification through dimethyl-aminoethanol.⁶ Reactive processing of many polymer-polymer blends, however, appeared in the literature recently. In general, chemical compatibilization in polymer blends was shown to take place with the help of the reactions between the following groups: anhydride or carboxyl with amine, oxazoline with carboxyl, epoxy with carboxyl or hydroxyl or anhydride, or amine and interchain salt formation.² The literature survey reveals that the scientific understanding of the compatibilization phenomena is still in the nascent state and a common mechanism is still obscure.

In addition, there are a large number of dissimilar rubber-plastic blends that have been discovered over the last decade. Compatibilization of these pairs is expected to enhance the properties and the performance of these blends. The combination of nylon/nitrile rubber is one such example.

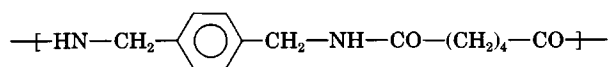
We have reported in our earlier communication various factors affecting the morphology of nylon/hydrogenated nitrile rubber (HNBR) blends.⁷ Nylons are attractive materials for scientific studies of reactive compatibilization due to their inherent chemical functionality through the amine or carboxyl end groups that may be present and, potentially, the amide linkage. In this work, we report our observations on the interfacial parameters and the morphology of a 50 : 50 nylon/HNBR blend with the addition of chemical compatibilizers like car-

boxy-terminated nitrile rubber (CTBN), amine-terminated nitrile rubber (ATBN), liquid carboxylated nitrile rubber (LXNBR), carboxylated nitrile rubber (XNBR), chlorovinylsilane (CIVSi), ethoxyvinylsilane (EtVSi), and maleic-modified HNBR (MA-HNBR). In the above series, the compatibilizer has one component that can react with the nylon phase and the other component can co-vulcanize with HNBR through a cross-linker.

EXPERIMENTAL

Materials

The elastomer used in this study was hydrogenated nitrile rubber (HNBR, Zetpol 1020, $T_g = -20^\circ\text{C}$, iodine value = 25, $M_n = 105,000$) obtained from Nippon Zeon Co., Japan. Nylon MXD6 ($T_g = 90^\circ\text{C}$, $T_m = 235^\circ\text{C}$, $M_n = 25,300$, and the structure as shown



was supplied by Mitsubishi Gas Chemical Co., Japan. All the nylon/HNBR blends under investigation contain a 50 : 50 plastic-to-rubber weight ratio. 2,5-Dimethyl(*t*-butyl peroxy) hexane was used as a cross-linker. Carboxy-terminated acrylonitrile butadiene (CTBN, 17.5 wt % ACN, $M_n = 3500$, obtained from B. F. Goodrich Co., U.S.A.), amine-terminated acrylonitrile butadiene (ATBN, 16.5 wt % ACN, $M_n = 3500$, obtained from B. F. Goodrich Co.), liquid carboxy-modified nitrile rubber (LXNBR, 20.0 wt % ACN, 0.08 equivalent phr carboxyl content, viscosity at $50^\circ\text{C} = 20,000$ cps, provided by Nippon Zeon Co., Japan), carboxylated nitrile rubber (XNBR, 0.08 equivalent phr carboxyl content, Nippon Zeon Co.), maleic-modified HNBR (MA-HNBR with 30% MA modification, prepared in the laboratory following the procedure given in Ref. 4), chlorovinylsilane (CIVSi), and ethoxyvinylsilane (EtVSi) (both obtained from Tokyo Chemical Industries, Japan) were chosen as compatibilizers.

Mixing

Melt-mixing of nylon/HNBR blends was carried out at 250°C at 100 rpm in a miniature mixing reactor as described earlier.⁷ Nylon was first melted at 250°C . The rubber premixed with 0.9 phr of the cross-linker was then added and the mixing continued for 16 min. A small amount of mixed melt from the mixing zone was taken out from time to time

and quenched in water to freeze the two-phase structure in the blend. The compatibilizer was used at various loadings (1, 3, and 5 parts per hundred grams of rubber, phr) and also added in different sequences. For example, in the majority of the mixes, unless otherwise mentioned, compatibilizers were first mixed with HNBR on a two-roll mill at room temperature, whereas for a few mixes, these were added in the nylon first. These are described later under separate sections.

Structure Analysis

The morphology of the blends was analyzed with the help of a light-scattering apparatus, described earlier,⁷ using a He—Ne laser of 6328 Å wavelength and under parallel polarization (V_V) alignment. The quenched specimen was placed between two cover glasses and melt-pressed to a thin film ($\sim 20 \mu\text{m}$) at 250°C on a hot stage and immediately subjected to a time-resolved light-scattering measurement with a time slice of 1/30 s. The morphology parameters were obtained from the Debye–Bueche plot of $I(q)^{-1/2}$ vs. q^2 [where $I(q)$ is the intensity of scattered light, and q , the magnitude of scattering vector] as shown below:

$$I(q)^{-1/2} = [8\pi\langle\eta^2\rangle\zeta^3]^{-1/2}[1 + \zeta^2q^2] \quad (1)$$

where $\langle\eta\rangle$ is the mean square fluctuation of the refractive index, and ζ , the correlation distance. The mean radius of the dispersed particle, \bar{R} , and the specific interfacial area, S_{sp} , were obtained from ζ and ϕ , the volume fraction of the dispersed phase, as follows:

$$S_{\text{sp}} = 4\phi(1 - \phi)\zeta^{-1} \quad (2)$$

$$\bar{R} = 3\phi S_{\text{sp}}^{-1} \quad (3)$$

The phase structure was analyzed under a light microscope (Olympus), a transmission electron microscope (TEM, Hitachi HT 300), and a scanning electron microscope (SEM, JEOL JSM T220). For light microscopy, the samples were melted at 250°C. For TEM observation, the rubber phase was stained with ruthenium tetroxide and the stained and hardened specimen was microtomed at -100°C to an ultrathin section of 70 nm thickness. For SEM observation, the sample was microtomed to prepare a flat surface and was stained with osmium tetroxide for 16 h at room temperature. The back-scattered electron image was recorded. FTIR studies were carried out using Shimadzu FTIR-8100 spectrometer on thin films prepared at 250°C in a hydraulic press.

Interfacial Parameters

Interfacial thickness between nylon and rubber was measured using an automated Ellipsometer (EL-8, Optec Co., light of 632.8 nm wavelength applied at an incident angle of 70°). For this experiment, nylon was first melt-pressed to form a flat and thick ($\sim 0.5 \text{ mm}$) substrate. Rubber with the required proportion of compatibilizer was dissolved in monochlorobenzene to make a 6% solution and filtered through a Millipore filter to remove dust. The filtered solution was then spin-coated onto nylon at room temperature. The bilayer specimen of nylon and rubber was then inserted into a hot chamber at 250°C in a nitrogen atmosphere for ellipsometric analysis to measure the retardation, Δ , and the reflection ratio, Ψ . For data analysis, a four-layer model, as reported in an earlier communication,⁸ was used (Fig. 1). Since the value of the refractive index, n_1 , n_2 , and n_4 , and the thickness, d_2 , were known, n_3 and d_3 could be estimated by selecting the best set of these values to fit the observed values of Δ and $\tan \Psi$ in the Drude equation as shown below:

$$\rho = \frac{R_m^p}{R_m^s} = \frac{|R_m^p| \exp(i\Delta p)}{|R_m^s| \exp(i\Delta s)} = \frac{|R_m^p|}{|R_m^s|} \exp[i(\Delta p - \Delta s)] = \tan \psi \exp(i\Delta) \quad (4)$$

$$R_m^r = \frac{r_m^r + R_{m+1}^r \exp(-iD_{m+1})}{1 + r_m^r R_{m+1}^r \exp(-iD_{m+1})} \quad (5)$$

$$D_m = 4\pi n_m d_m (\cos \theta_m) / \lambda' \quad (6)$$

$$r_m^p = \frac{n_{m+1} \cos \theta_m - n_m \cos \theta_{m+1}}{n_{m+1} \cos \theta_m + n_m \cos \theta_{m+1}} \quad (7)$$

$$r_m^s = \frac{n_m \cos \theta_m - n_{m+1} \cos \theta_{m+1}}{n_m \cos \theta_m + n_{m+1} \cos \theta_{m+1}} \quad (8)$$

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 = n_3 \sin \theta_3 = n_4 \sin \theta_4 \quad (9)$$

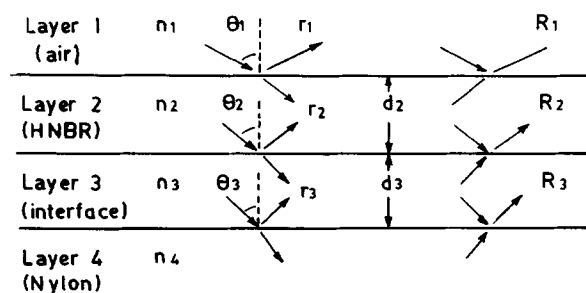


Figure 1 Four-layer model for ellipsometric analysis.

where ρ is the relative amplitude of parallel (R_m^p) to perpendicular (R_m^s) reflection coefficients in the incident plane, n_m and d_m represent the refractive index and the thickness of the m^{th} layer, respectively, and r_m is the Fresnel reflection coefficient at the boundary between m^{th} and $(m + 1)^{\text{th}}$ layers. Numerical calculation was carried out by a Hitachi Computer, Hitac M 660K.

RESULTS AND DISCUSSION

Interfacial Parameters

The effect of various compatibilizers on the interfacial thickness is shown in Figures 2 and 3 and Table I. The interfacial thickness between nylon and HNBR vulcanized *in situ* was 48 nm. Addition of the 3 phr CTBN compatibilizer increased the thickness to 73 ± 2 nm (Fig. 2). It was interesting that the thickness gradually increased in the initial stage and leveled off at the later stages. ATBN showed a similar trend and an interfacial thickness of 76 nm was attained at the late stages (Table I). In contrast, the results of LXNBR and CIVSi at similar concentrations indicated a rapid formation of thick interface (even before 1 min). At the 3 phr level, the interfacial thickness of the sample containing LXNBR was slightly higher than that of other samples as shown in Table I and Figure 3. CTBN, ATBN, and CIVSi at the same level gave roughly similar values.

Though the reactivity of various compatibilizers toward nylon and HNBR is expected to be different

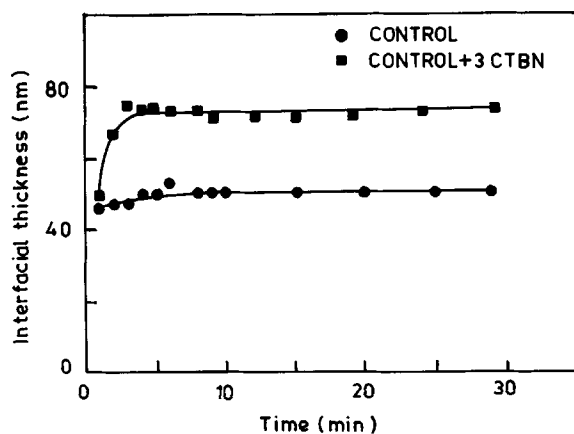


Figure 2 Time variation of interfacial thickness at 250°C: (●) bilayer specimen of nylon and HNBR premixed with 0.9 phr cross-linker; (■) bilayer specimen of nylon and HNBR premixed with 0.9 phr cross-linker and 3 phr CTBN.

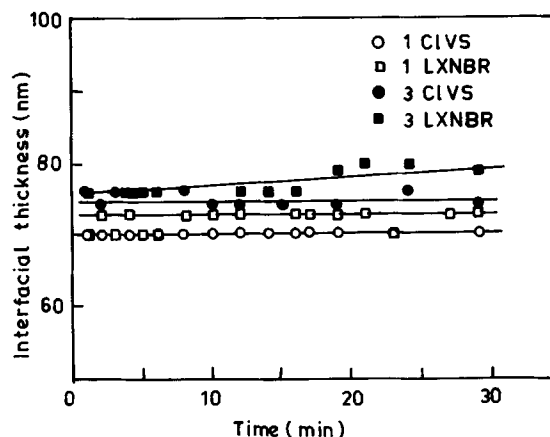


Figure 3 Time variation of interfacial thickness at 250°C: (○) nylon and HNBR premixed with 0.9 phr cross-linker and 1 phr chlorovinylsilane; (□) nylon and HNBR premixed with 0.9 phr cross-linker and 1 phr LXNBR; (●) nylon and HNBR premixed with 0.9 phr cross-linker and 3 phr chlorovinylsilane; (■) nylon and HNBR premixed with 0.9 phr cross-linker and 3 phr LXNBR.

because of the nature of the reactive groups, the attainable interfacial thickness is, however, comparable (due to high reactivity at the high temperature of measurement). The compatibilizers were added

Table I Values of Interfacial Thickness, Interfacial Tension, and Interaction Parameter

System	λ (nm)	$\chi_{PR} \times 10^3$	$\gamma_{\infty} \times 10$ (mN/m)
Control	48	2.80	2.40
Control + 1 phr LXNBR	72 ± 1	2.01	2.06
Control + 3 phr LXNBR	79 ± 2	1.87	1.98
Control + 5 phr LXNBR	ca. 70	2.06	2.09
Control + 3 phr CTBN	73 ± 2	1.99	2.05
Control + 3 phr ATBN	76	1.93	2.02
Control + 1 phr CIVSi	70	2.06	2.09
Control + 3 phr CIVSi	75	1.95	2.03
Control + 5 phr CIVSi	76	1.93	2.02
Control + 3 phr XNBR	50	2.68	2.38

Control means bilayer specimen of nylon and HNBR mixed with 0.9 phr cross-linker. Compatibilizers were added always in the rubber phase.

in different proportions in the rubber and their effect on interfacial thickness was also studied (Table I and Fig. 3). The interfacial thickness increased gradually with the increase in the concentration of CIVSi and finally attained a constant value (76 nm) at the 5 phr level. It was interesting that a high value of interfacial thickness (70 nm) was obtained even with 1 phr concentration of the compatibilizer. For bilayer specimens containing LXNBR, however, there was an optimum value at 3 phr. The interfacial thickness decreased at 5 phr level (Table I). A higher amount of LXNBR at the interface is likely to cause clustering of the ions, preventing them from further reaction and thereby reducing interfacial thickness. It was demonstrated before that the physical compatibilizer acts as a surfactant between the polymers and reduces interfacial tension.¹ There must be a certain quantity of surfactant required for saturation of the interface. It was shown for oil/water emulsion that the addition of surfactant beyond an optimum concentration did not give rise to the desired effect.⁹

The interfacial tension (γ_∞) and the interaction parameter (χ_{PR}) were calculated from the measured values of the interfacial thickness, λ , and the Kuhn segment length, a ($= 0.8$ nm), using the following equations¹⁰:

$$\lambda = \frac{2a}{(6\chi_{PR})^{1/2}} \left[1 + \ln 2 \left(\frac{1}{\chi_{PR}N_R} + \frac{1}{\chi_{PR}N_P} \right) \right] \quad (10)$$

$$\gamma_\infty = \frac{kT}{a^2} \left(\frac{\chi_{PR}}{6} \right)^{1/2} \quad (11)$$

where N_R and N_P are the number of segments of the rubber and the plastic, respectively. As shown in Table I, the interfacial tension was considerably reduced with the addition of the compatibilizers. For example, γ_∞ of the specimen containing 3 phr LXNBR was 0.198 mN/m as compared to a value of 0.240 mN/m of the control (without compatibilizer). This reduction was greater when the concentration of the compatibilizer was higher (cf. 1 and 3 phr LXNBR; 1, 3, and 5 phr CIVSi; Table I). The interaction parameter accordingly decreased, e.g., from 2.80×10^{-3} to 1.87×10^{-3} for a 3 phr LXNBR system. Since the interaction parameter between a polymer pair is constant at a constant temperature, this simply means that the polymer pair interacts in such a way in the presence of the compatibilizers as if the interaction parameter is reduced. It is very clear from the results that the increase in interfacial thickness is due to the reduction of interfacial tension and the chemical compatibilizer in this sense also behaves as a reactive surfactant in the present investigation.

It is interesting to note that an interfacial thickness of 70 nm or more is obtained with the use of compatibilizers. The values in Table I (excepting the control and the XNBR system) are about five times more than the root mean square end-to-end distance of nylon (15 nm, estimated by using $\langle r_0^2 \rangle^{1/2} = 10.0 \times 10^{-2} M^{1/2}$ [Ref. 11]) and three times more than the average end-to-end distance of HNBR (26 nm, estimated from $\langle r_0^2 \rangle^{1/2} = 8.0 \times 10^{-2} M^{1/2}$ [Ref. 11]). Even in a system without a compatibilizer, this is roughly two to three times more than the end-to-end distance of nylon or HNBR. This can only be possible when nylon reacts with rubber in the presence of the cross-linker to form a graft copolymer. Free-radical grafting onto nylon was recently pointed out by Leibler and Lambla.¹² Also, in our earlier communication, we presented evidence of degradation of nylon and HNBR from the rheometric studies at 250°C.⁷ It was pointed out that the interfacial thickness should increase twofold when a block or graft copolymer, A—B, locates at the interface between immiscible polymers A and B and the interfacial thickness in the neat A—B block copolymer is about five times the value between A and B.¹³ But these values are still smaller than the coil size of the component polymers. Yukioka and Inoue¹⁴ reported an interfacial thickness of 50 nm between amorphous polyamide and poly(styrene-*co*-acrylonitrile) with the addition of 20 wt % poly(styrene-*co*-maleic anhydride), which acted as a compatibilizer in the system. The value was about 10 times more than the control and the results were similar to those in the present investigation.

There are two phenomena that seem to be important in the mechanism of reactive compatibilization:

1. Diffusion at the interface of the polymer pair and the role played by the compatibilizers.
2. Reaction between the polymer pair and the effect of the compatibilizers on the interlinking process.

To separate the effect of these two processes, a bilayer specimen was prepared using solid XNBR as the compatibilizer in place of LXNBR. It was observed from Table I that the thickness of the interface did not change much with the addition of 3 phr XNBR as compared to that of control. Hence, it is clear that the diffusion at the interface is important even when there is a reactive compatibilizer. The high molecular weight XNBR cannot diffuse as rapidly as can low molecular weight LXNBR. The

interdiffusion must depend on both a thermodynamic term that involves the Gibbs free energy of mixing and a mobility term determined by interdiffusion of the component polymers. It may be further hypothesized that the situation must be created at the interface so that the reaction and diffusion or vice versa take place continuously and the reactive compatibilizer from the bulk must be driven toward the interface. Or, in other words, continuous refreshing of the interface is necessary to reduce the interfacial tension and increase the thickness. In the mutual penetration of two miscible polymers, it was shown that the diffusion takes place faster when the thermodynamic driving force for dissolution $|\chi - \chi_c|$ was larger (where χ_c is the Flory interaction parameter at the critical point).⁸ Such an analogy could not be drawn for the present immiscible pair. However, it was observed from Table I that the compatibilizers lowered the value of apparent χ and brought these closer to the value of χ_c calculated from the following relation:

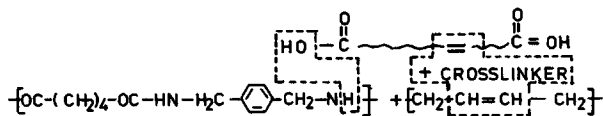
$$\chi_c = \frac{1}{2} (N_P^{-1/2} + N_R^{-1/2})^2 \quad (12)$$

Since there was a rapid interface formation for most of the combinations, it was difficult to obtain an accurate value of the diffusion coefficient. However, for the CTBN and ATBN systems, the diffusion constant, D , estimated from the plot of λ^2 vs. time t in the region $t \ll t_{\text{plateau}}$ using the following equation⁸:

$$\lambda^2 = 2(Dt)^{1/2} \quad (13)$$

was of the order of $8\text{--}9 \times 10^{-14} \text{ cm}^2/\text{s}$ at 250°C .

The compatibilizers in the present investigation are expected to react with nylon and HNBR. The reaction may be visualized for CTBN system as follows:



Other compatibilizers would follow a similar trend. For example, the amine group of the ATBN may react with the acid group of nylon and the double bonds of ATBN and HNBR may be reactive in presence of 2,5 dimethyl(*t*-butyl peroxy) hexane. Similarly, the Cl group of CIVSi should be reactive toward nylon, and the vinyl group may be joined with HNBR with the help of the cross-linker. Additionally, amide linkage may be used up for the reaction. The free radicals generated by degradation

of nylon and HNBR^{15,16} at a high temperature of 250°C may participate in the reaction. FTIR spectra of blend of nylon and HNBR showed very complicated features. There was a peak at 1635 cm^{-1} characteristic of the —NH deformation vibration for the control blend. On reaction with a compatibilizer like LXNBR, its peak area calculated with respect to the —CH stretching vibration at 1420 cm^{-1} increased from 0.79 to 0.90. There was also a new peak appearing at 1680 cm^{-1} , characteristic of the —C=O stretching vibration:amide I band for the compatibilized systems. The efficiency of the reaction with LXNBR, based on the measurement of the peak area at 1635 and 1680 cm^{-1} , is higher than that with CTBN. This observation is in line with the interfacial thickness obtained.

Structure Parameters

Reactive processing of the rubber–plastic blends in presence of the compatibilizers was carried out and the structure parameters, i.e., mean radius of the dispersed particle (\bar{R}), specific interfacial area (S_{sp}), and the correlation distance (ζ) were determined. Figure 4 shows a typical Debye–Bueche plot of $I(q)^{-1/2}$ against q^2 of a 50 : 50 compatibilized blend [eq. (1)]. The correlation distance was obtained from the slope and the intercept of the plot. Other morphology parameters, \bar{R} and S_{sp} , were obtained from eqs. (2) and (3). Since in the present experiment we have noted a distinct change in the behavior of the blends with the sequence of the addition of

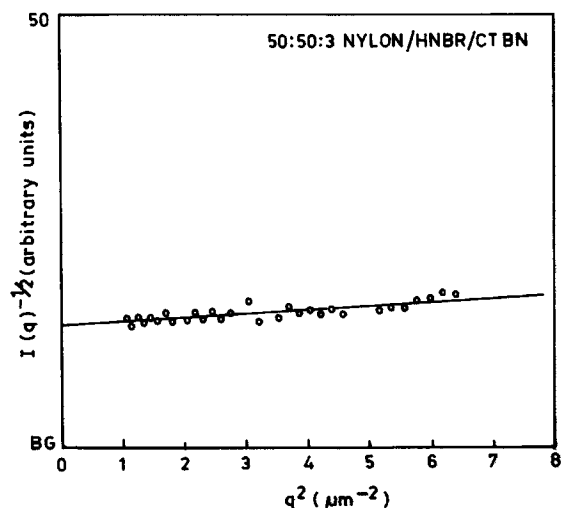


Figure 4 An example of Debye–Bueche plot of $I(q)^{-1/2}$ vs. q^2 for a 50 : 50 dynamically vulcanized nylon/ (HNBR premixed with 3 phr CTBN and 0.9 phr cross-linker) blend (mixing time 10 min at 250°C).

the compatibilizers, the following discussion is divided into two parts.

Process A: Compatibilizer Added in HNBR Phase, Premixed with the Cross-Linker, on a Two-Roll Mixing Mill, and the Mixture Then Blended with Nylon

The effect of mixing time on ζ , S_{sp} , and \bar{R} is shown in Figure 5. It was observed that the particle size decreased with the mixing time, attained a minimum value, and then increased. The correlation distance followed exactly the same trend. S_{sp} , however, increased with mixing time and then decreased after the maximum. The systems with and without compatibilizers showed the above general behavior. The particle size developed was lower than that reported for similar rubber-plastic blends,³ which might be due to the graft reaction between nylon and rubber and the compatibilizing action. Addition of compatibilizers, however, had two significant effects: (1) the compatibilizers reduced the particle size and the correlation distance over the whole range of mixing times, as compared to the control system and (2) the reduction took place in the very early stage even before 2 min of mixing (Fig. 5). For example, at 2 min of mixing, the particle size of a 3 phr LXNBR compatibilized blend was 0.35 μm , whereas the same was 0.73 μm for the control. It was also interesting that \bar{R} of the compatibilized system remained constant for a certain period of time before the final increase. The increase in particle size after 10 min of mixing at 250°C was also less with the compatibilized system. S_{sp} increased with the addition of the compatibilizers and showed a maximum value of 6.53 μm^{-1} with 3 phr CTBN and CIVSi. The particle size was reduced with the increased compatibilizer concentration up to a certain level. For example, the 3 phr LXNBR compatibilized blend showed a lower value of \bar{R} than that of the blend containing 1 phr LXNBR (Fig. 5). However, at 5 phr of the compatibilizer, \bar{R} did not change further and there was a tendency for \bar{R} to increase. The morphology parameters at 10 min mixing time at 250°C for various systems are reported in Table II. All compatibilized systems at certain concentrations showed lower values of \bar{R} than did the control. However, it was difficult to correlate the particle size with the structure and reactivity of the compatibilizer at similar concentrations.

To elucidate the structure more elaborately, TEM studies were undertaken. A representative photomicrograph (Fig. 6) shows the size and the shape of the dispersed particle of a 3 phr CTBN compatibil-

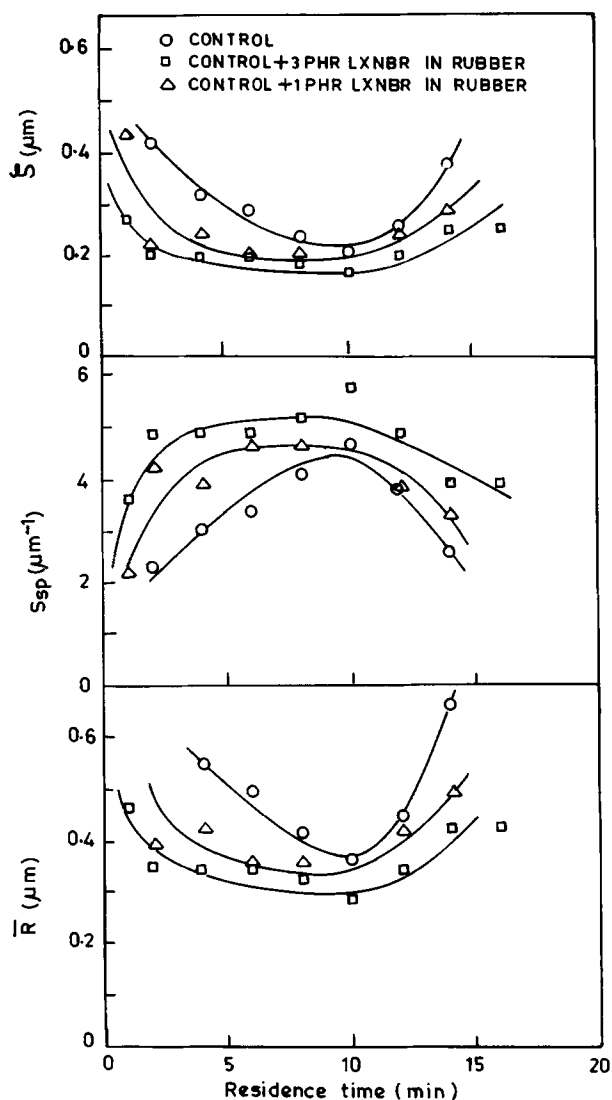


Figure 5 Time variation of morphology parameters during melt-mixing at 250°C for (O) 50 : 50 nylon/HNBR premixed with 0.9 phr cross-linker; (Δ) 50 : 50 nylon/HNBR premixed with 0.9 phr cross-linker and 1 phr LXNBR; (\square) 50 : 50 nylon/HNBR premixed with 0.9 phr cross-linker and 3 phr LXNBR.

ized blend. TEM observations corroborate the light-scattering studies in general.

The interfacial thickness, as discussed in an earlier section, was maximum at 3 phr LXNBR concentration. Other compatibilizers also increased the thickness and lowered the interfacial tension at a similar concentration. It is clear that the reduction of particle size is due to the ability of the compatibilizers to behave as a surfactant and to reduce the interfacial tension between the dispersed phase and the matrix. Extending Taylor's criteria to the case

Table II Structure Parameters at 10 Min Mixing Time at 250°C for Samples Having Various Compatibilizers

Sample	ζ (μm)	\bar{R} (μm)	S_{sp} (μm^{-1})	$V_{\lambda} \times 10$
Control	0.21	0.36	4.66	2.24
A ₁ (control + 3 phr CTBN)	0.17	0.29	5.76	4.21
A ₂ (control + 3 phr ATBN)	0.19	0.33	5.15	3.91
A ₃ (control + 3 phr CIVSi)	0.16	0.26	6.53	4.90
A ₄ (control + 3 phr LXNBR)	0.17	0.29	5.76	4.55
A ₅ (control + 5 phr LXNBR)	0.22	0.38	4.45	3.11
B ₁ (control + 3 phr CTBN)	0.76	1.32	1.29	0.94
B ₂ (control + 3 phr LXNBR)	0.35	0.60	2.85	2.25
B ₃ (control + 3 phr XNBR)	0.23	0.40	4.26	2.13
B ₄ (control + 3 phr EVS)	0.42	0.73	2.33	—
B ₅ (control + 10% MA-HNBR)	0.43	0.75	2.28	—
B ₆ (control + 5 phr EVS)	0.41	0.71	2.39	—

Control means HNBR premixed with cross-linker added to the nylon. In all A samples, the compatibilizer was mixed with rubber and peroxide first and then the mixture was added to the nylon. In all B samples, the compatibilizer was mixed with nylon first and then the rubber premixed with peroxide was added to the mixer.

of viscoelastic drop in a viscoelastic matrix, Wu proposed a relationship between the number-average particle diameter ($2\bar{R}$), viscosity of the dispersed phase (η_d) and the matrix (η_m), interfacial tension (γ_{∞}), and effective shear rate (S_R) of the mixer as follows¹⁷:

$$2\bar{R} = 4(\eta_d/\eta_m)^{0.84}\gamma_{\infty}/S_R\eta_m \quad \text{for } \eta_d > \eta_m \quad (14)$$

Designating the control system with suffix 1 and the compatibilized system with suffix 2, eq. (14) reduces to

$$(\bar{R}_1/\bar{R}_2) = (\gamma_{\infty 1}/\gamma_{\infty 2}) \quad (15)$$

assuming that a small amount of compatibilizer does

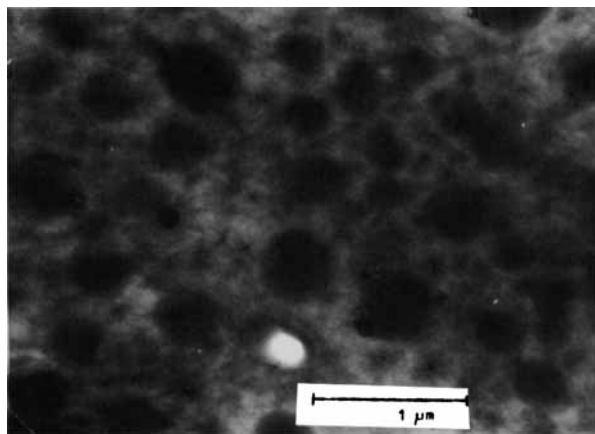


Figure 6 Transmission electron micrograph of a 50 : 50 blend of nylon/HNBR premixed with 0.9 phr cross-linker and 3 phr CTBN (8 min mixing time at 250°C).

not change η_d and η_m significantly. From eq. (15), a reduction in $\gamma_{\infty 2}$ would reduce \bar{R}_2 or the particle size of the compatibilized system. However, the calculated values of \bar{R}_2 from eq. (15) and Table I are not in exact accord with the measured values. For example, chlorovinylsilane (3 phr) and CTBN (3 phr) showed lower experimental values of \bar{R}_2 , whereas ATBN (3 phr) and LXNBR (3 phr) displayed higher values than the calculated ones. This means that such changes in the dispersed particle size cannot be explained quantitatively by the changes in γ_{∞} alone. Complex rheological forces responsible for the breaking down of particles, creation of mobile interface, and stabilization of particles through the addition of a compatibilizer may be a part of the mechanism. However, in the absence of any theory taking the above factors in mind, Wu's equations for understanding the particle-size reduction for a compatibilized system are a good guide. It can also be envisaged from eq. (14) that there is a critical value defined by $\eta_m S_R 2\bar{R}/\gamma_{\infty}$, called the Weber number, i.e., the ratio of viscous force to interfacial force for a particular polymer pair at which a critical particle size would result and the compatibilizer would saturate the interface. Addition of compatibilizer beyond this concentration should not give rise to further particle-size reduction. For an ion-containing compatibilizer added in an excess quantity, there may be a deleterious effect from the aggregation of the dispersed particles or ion clustering. Such a phenomenon was reported for polyethylene and polyamide blends with a high concentration of ionomer.¹⁸

Multiplying the interfacial thickness (λ) by the specific interfacial area (S_{sp}), one can obtain the volume fraction of the interface (V_i). The values are shown in Table II. It was clear that the volume fraction of the interface increased with the addition of the compatibilizers. The values are almost double than that of the control blend.

Process B: Compatibilizer Added in the Nylon Phase and the Rubber, Premixed with the Cross-linker, and Blended

A few rubber-plastic blends were studied by changing the sequence of compatibilization, i.e., the compatibilizer was added in the nylon phase before

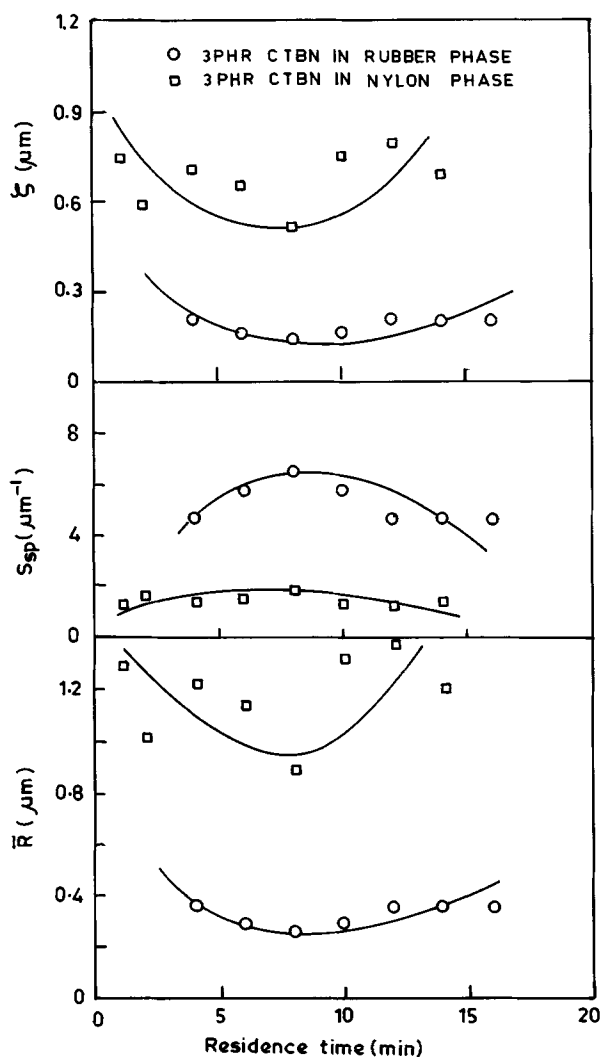


Figure 7 Time variation of the morphology parameters at 250°C mixing temperature for nylon/HNBR premixed with 0.9 phr cross-linker and 3 phr CTBN added first either in the rubber phase or in the nylon phase.

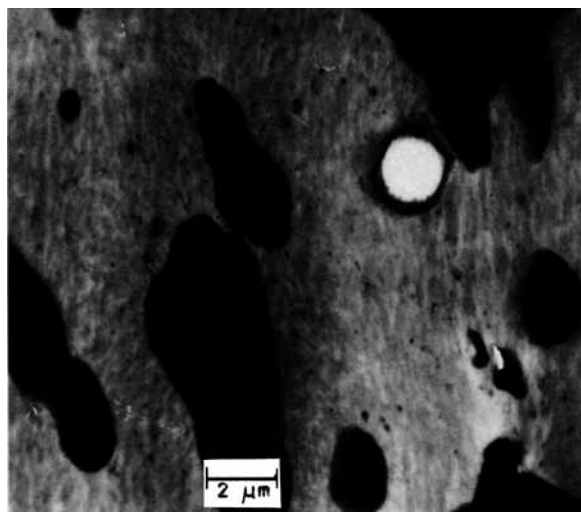


Figure 8 Transmission electron micrograph of a 50 : 50 blend of nylon + ATBN/HNBR premixed with 0.9 phr cross-linker (mixing time 10 min at 250°C).

blending with rubber. The results are shown in Figure 7 and Table II and compared with those discussed in the earlier part. The time variation of the morphology parameters, ζ , \bar{R} , and S_{sp} , was very similar. \bar{R} and ζ decreased in the initial stage and then increased after a minimum was obtained. But the values of \bar{R} and ζ were considerably higher in this process of mixing. The mean radius of the dispersed particle at 10 min of mixing at 250°C was two to three times larger (Table II). It was interesting that these values were even higher than that of the control system. Accordingly, S_{sp} for the compatibilized blends (Process B) was rather low. To demonstrate further, transmission electron micrographs were taken. An example is shown in Figure 8. Many particles were very large, shifting the average diameter to the higher side. Cimmino et al.¹⁹ made similar observations with nylon/EPDM blends. Willis and Favis¹⁸ reported for the polyamide/polyethylene system with an ionomeric compatibilizer that preblending the nylon-dispersed phase with the ionomer increased the particle size by an average of 68% relative to one-step mixing. They postulated that the affinity of the ionomer for nylon would ensure a random distribution of the ionomer within the nylon-dispersed phase rather than a high concentration of the ionomer at the polyolefin/nylon interface. A similar mechanism may be true in the present system. Also, since the compatibilizers have greater affinity for nylon, mixing nylon with the compatibilizer would cause a fast reaction between them and a gelled product, which would phase-separate and would not be effective as

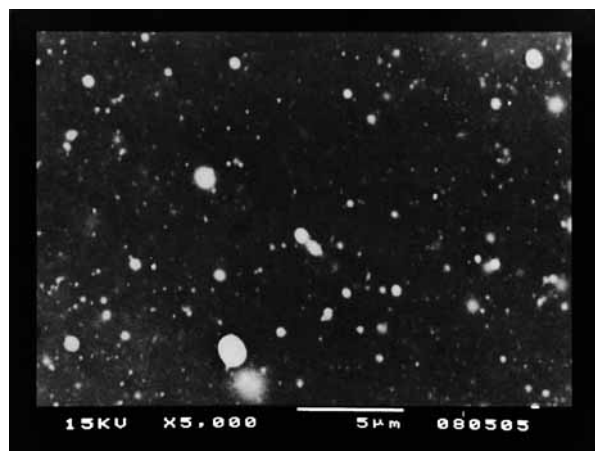


Figure 9 Scanning electron micrograph of a blend of 3% CTBN with nylon.

a surfactant. To prove this, 3 phr CTBN was mixed with nylon in the same way and the morphology was examined under the SEM (Fig. 9). It was clear that even at low concentration they form a fine dispersed phase, which would presumably not act like surfactant. It is also possible that such a mechanism may operate when an excess quantity of the compatibilizers are added even in the mixing procedure A. It was probably another reason why addition of 5 phr of CTBN/LXNBR generated a larger diameter of the dispersed phase.

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