

Structure Development during Dynamic Vulcanization of Hydrogenated Nitrile Rubber/Nylon Blends

ANIL K. BHOWMICK* and TAKASHI INOUE

Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan

SYNOPSIS

The factors that influence the morphology and the interfacial parameters during dynamic vulcanization of hydrogenated nitrile rubber/nylon blends are examined. The particle size of the dispersed phase (\bar{R}) and the correlation distance (ξ) of a 50 : 50 blend decreased with increasing mixing time at 250°C, attained a minimum value, and then increased. The increase in the number of particles with time (dn/dt) may be expressed as $(dn/dt) = k'n^m$, where n is the number of dispersed particles at time t , and m and k' are constants. \bar{R} and ξ gradually increased as the mixing temperature was increased from 250 to 300°C at a constant mixing time of 10 min. The particle size increased also with the increasing gel fraction of the rubber. At a constant mixing time of 10 min at 250°C, the particles were larger when the addition of the cross-linker was delayed. These observations can be explained with the help of a hypothetical model, similar to that proposed by Wu, considering the breaking down of rubber particles, coagulation and coalescence of droplets, and droplet rupture in a matrix of nylon. On vulcanization, the thickness of the interface (λ) reduced from 62 to 48 nm. The interaction parameter and interfacial tension, as estimated from λ , for a bilayer specimen vulcanized *in situ* at 250°C were 2.8×10^{-3} and 0.24 mN/m, respectively. The high value of λ for the dissimilar polymer pair may be due to polymer-polymer graft formation at high temperature. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Dynamic vulcanization is a process of cross-linking the elastomeric phase during melt mixing of a rigid thermoplastic with a soft elastomer. It provides a number of performance advantages over their non-vulcanized counterpart, especially for thermoplastic elastomeric rubber-plastic blends. Coran¹ described the preparation and the properties of various elastomer-plastic blends. Melt mixing of the polymer pair was followed by the addition of a suitable cross-linking system for the elastomer during dynamic vulcanization. Other workers²⁻⁴ also reported their results of dynamically vulcanized rubber-plastic blends. The properties of these two-phase polymer

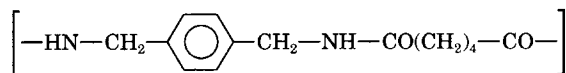
blends depend on the properties of the individual phases, adhesion between components, and, most importantly, the phase morphology of the system. The previous studies, however, have not highlighted the structure development during intensive mixing and dynamic vulcanization. These studies are very important when the two polymers differ widely in chemical composition, polarity, and solubility parameter and also when the mixing and vulcanization of rubber are carried out at a high temperature ($> 200^\circ\text{C}$). Only recently, Okamoto and Inoue⁵ discussed the importance of structure development in a blend of poly(ϵ -caprolactone) and hydrogenated nitrile rubber and concluded that phase inversion takes place at a certain critical viscosity of rubber when the rubber particles begin to coagulate with each other in low-viscosity plastic. The purpose of the present investigation was to understand the factors that influence the structure development in two-phase elastomer-plastic blends. Two dissimilar polymers—a special grade nylon and a hydrogenated

* To whom correspondence should be addressed. On leave from the Indian Institute of Technology, Kharagpur, India.

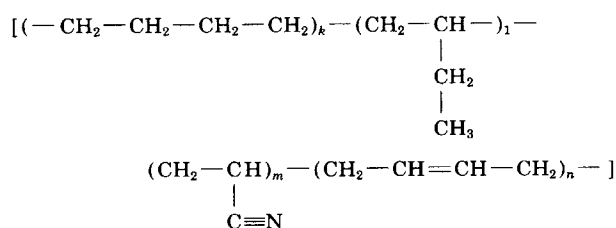
nitrile rubber (HNBR)—were selected for this study.

EXPERIMENTAL

Compositions were prepared from nylon MXD 6 ($M_n = 25300$; $T_g = 90^\circ\text{C}$; $T_m = 235^\circ\text{C}$):



supplied by Mitsubishi Gas Chemical Co., Japan, and HNBR (Zetpol 1020; $T_g = -20^\circ\text{C}$; iodine value = 25, $M_n = 105,000$):



obtained from Nippon Zeon Co., Japan. 2,5-Dimethyl(*t*-butyl peroxy)hexane was used as cross-linker.

Melt mixing of nylon–rubber blends was carried out at 250°C at a rotor speed of 100 rpm in a miniature mixing reactor (Conerder, Tosoku Seimitsu Ltd). Nylon was first melted. For uncross-linked blends, rubber was then added in the desired weight ratio. For dynamically vulcanized blends, the rubber, premixed with 0.9 phr of the cross-linker on a two-roll mill, was incorporated. In one study only, the cross-linker was added in the mixer at 250°C at various times. A few mixes were carried out with various dosages of the cross-linker and also at different temperatures (240, 270, and 300°C). After the blending, the melt was quickly quenched in water to freeze the two-phase structure in the blend. A small amount of mixed melt (extrudate) was taken out from time to time and quenched in water for studies of structure development.

Structure development was investigated by using the light-scattering apparatus shown in Figure 1. The quenched specimen was placed between two cover glasses and melt-pressed to a thin film (ca. 20 μm) 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 using a He–Ne Laser of 6328 \AA wavelength. The scattering profile was observed under V_v (parallel polarization) alignment.

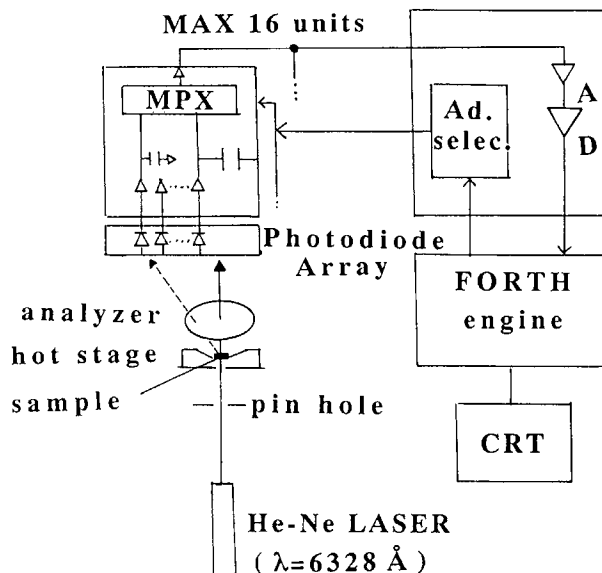


Figure 1 Light-scattering photometer equipped with 46 photodiode array for time-resolved measurement of angular dependence of scattered light intensity.

The two-phase structure in the melt-pressed state was also observed under a light microscope (Olympus). The samples were further examined under a transmission electron microscope (Hitachi HT-300) after staining the rubber phase with ruthenium tetroxide to enhance contrast between the phases.

The viscoelastic properties of nylon and uncross-linked and cross-linked rubbers were measured using a Dynamic Spectrometer (Rheometrics, USA). For measurement of the gel fraction, only the rubber was mixed with the required dosage of cross-linker on an open roll mill and then cured at 250°C for 10 min under pressure in a hydraulic press. A portion of these samples was immersed in monochlorobenzene for 48 h at 25°C . The gel fraction was calculated from the weights before and after swelling.

A bilayer specimen was prepared to investigate the interface between nylon and rubber. Nylon was first melt-pressed to form a flat and thick (ca. 0.5 mm) substrate. Rubber was dissolved in monochlorobenzene to make a 6% solution and filtered through a millipore filter to remove dust. The filtered solution was 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 . A detailed procedure for measurement and calculation of thickness was given in an earlier paper.⁶ Nylon (2% solution in formic acid) and rubber (1.5% solution in monochlorobenzene) were spin-coated

on a silicon wafer to measure the refractive index at different temperatures.

RESULTS AND DISCUSSION

Structure development was studied by the light-scattering method. The intensity of scattered light from the samples decreased monotonously with increasing scattering angle. The morphology parameters were obtained from the Debye-Bueche plot of $I(q)^{-1/2}$ vs. q^2 , where $I(q)$ was the intensity of scattered light, and q , the magnitude of the scattering vector.⁷ A Debye-Bueche plot of a representative dynamically vulcanized sample is shown in Figure 2. $I(q)^{-1/2}$ increases linearly with q^2 in accord with the following equation:

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

where $\langle \eta^2 \rangle$ is the mean-square fluctuation of the refractive index; and ξ , the correlation distance. ξ can be obtained from the slope and intercept of the $I(q)^{-1/2}$ axis (Fig. 2). Other morphology parameters such as the mean radius of the dispersed particles \bar{R} and the specific interfacial area S_{sp} are obtained from ξ as follows:

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

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

where ϕ is the volume fraction of the dispersed phase.

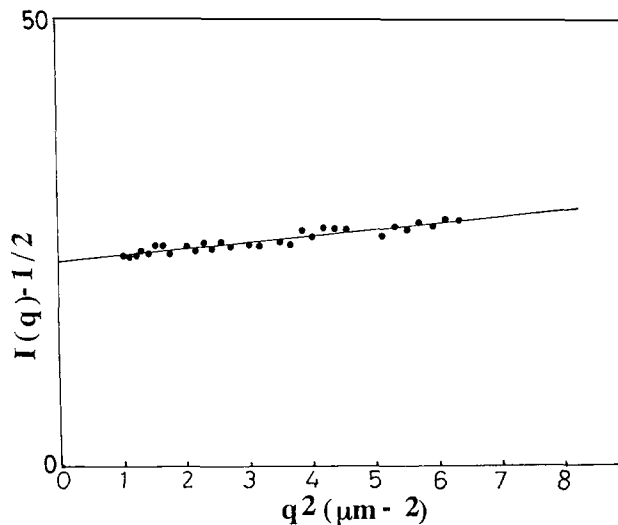


Figure 2 An example of a Debye-Bueche plot of $I(q)^{-1/2}$ vs. q^2 for a 50/50 dynamically vulcanized nylon-HNBR system (mixing time = 10 min at 250°C).

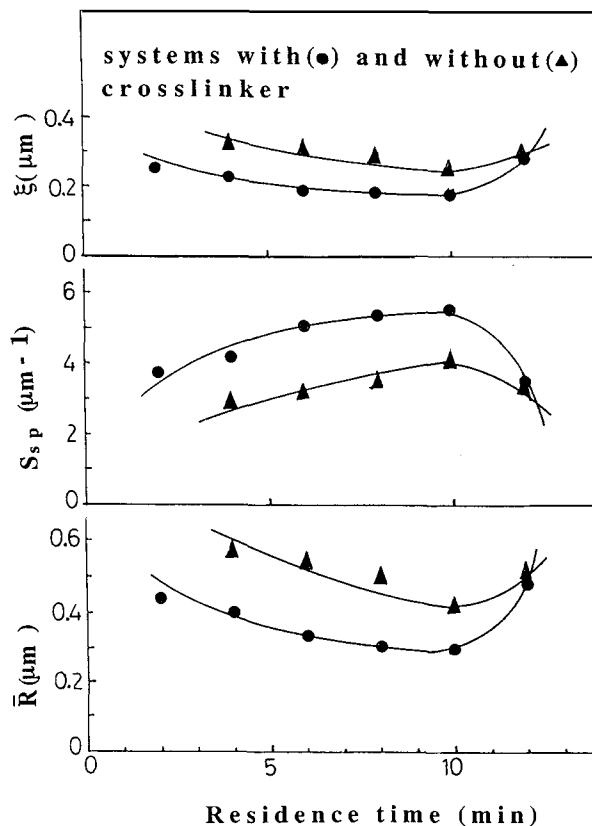


Figure 3 Time variation of morphology parameters during melt mixing at 250°C for 50/50 nylon/HNBR blends.

Effect of Mixing Time

The effect of mixing time on morphology parameters ξ , S_{sp} , and \bar{R} is shown in Figure 3 for a 50/50 nylon/HNBR system. The particle size decreases with increasing mixing time at 250°C and attains a minimum value at 10 min. The particle sizes are 0.31 and 0.40 μm for cross-linked and uncrosslinked systems, respectively. The particle size increases after 10 min. The correlation distance follows exactly the same pattern. The minimum correlation distance obtained at 10 min at 250°C for a vulcanized system is 0.18 μm . The specific interfacial area S_{sp} , however, increases with time up to about 10 min [$S_{sp}(\text{maximum}) = 5.45 \mu\text{m}^{-1}$; Fig. 3] and then decreases. A similar trend was obtained by Okamoto and Inoue⁵ for dynamically vulcanized poly(ξ -caprolactone) and nitrile rubber blends at 40/60 and 65/35 weight ratios. All the results could be explained with the help of a drop breakup mechanism discussed below.

The increase in the number of particles with mixing time (dn/dt) under a given condition may be expressed as

$$\frac{dn}{dt} = k'n^m \quad (4)$$

where n is the total number of dispersed particles at time t ; k' , the specific rate constant; and m , the order of the breakdown process. Equation (4) should be applicable to the dynamically vulcanized systems, as the results in Figure 3 indicate a breakdown process and the coalescence of particles may be assumed to be negligible.

Equation (4) reduces to eq. (5) on integration:

$$(-m + 1)\ln n = \ln(1 - m)k' + \ln t \quad (5)$$

assuming that the number of dispersed particles is zero at $t = 0$. Since the number of dispersed particles is proportional to the specific interfacial area, S_{sp} , eq. (5) may be further recast:

$$(-m + 1)\ln S_{sp} = \ln(1 - m)k'' + \ln t \quad (6)$$

Figure 4 shows a plot of $\ln S_{sp}$ vs. \ln residence time, t , up to 10 min (coagulation takes place after this). A straight-line relationship between these parameters suggests the applicability of eq. (6). The value of m obtained from the slope is 0.7, indicating that the order of the breakdown process is less than unity.

The morphology of the blends was also examined under an optical microscope and a transmission electron microscope (TEM). These studies corroborate the size-reduction process and confirm that the particle size is indeed smaller in the case of the dynamically vulcanized system. Photograph 1 reveals the morphology of a 50/50 dynamically vulcanized blend under a TEM. The black particles are RuO_4 -stained rubber. The number-average particle size of the dispersed phase corresponds roughly with the results obtained from the light-scattering method.

The results discussed above can be explained by considering rubber particles breaking down to form droplets in a continuous matrix of nylon (Fig. 5). Taylor⁸ established the condition for drop breakup in a Couette flow for an initially spherical Newtonian drop suspended in a Newtonian matrix. Cox⁹ discussed deformation and orientation of the droplets by considering both the effect of the viscosity difference and interfacial tension and predicted that the orientation angle ϕ tends to $\pi/4$ when the interfacial tension is dominant and $\phi \rightarrow \pi/2$ when the viscosity is dominant. Wu¹⁰ extended Taylor's criteria to the viscoelastic drop in a viscoelastic matrix and expressed particle size in terms of viscosity of the matrix and the dispersed phase, interfacial

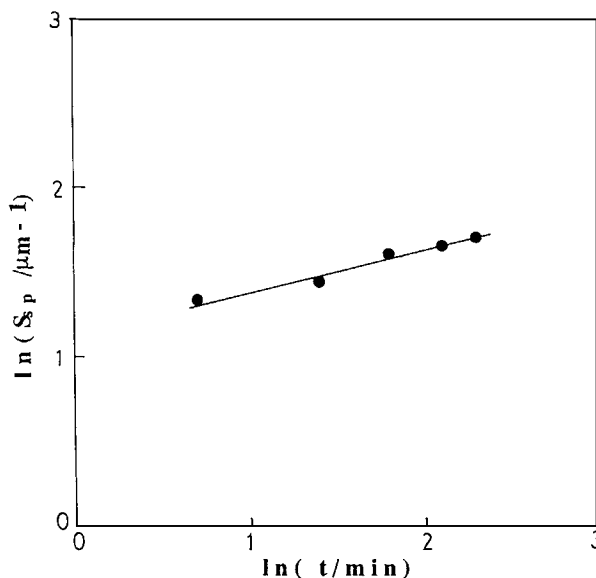


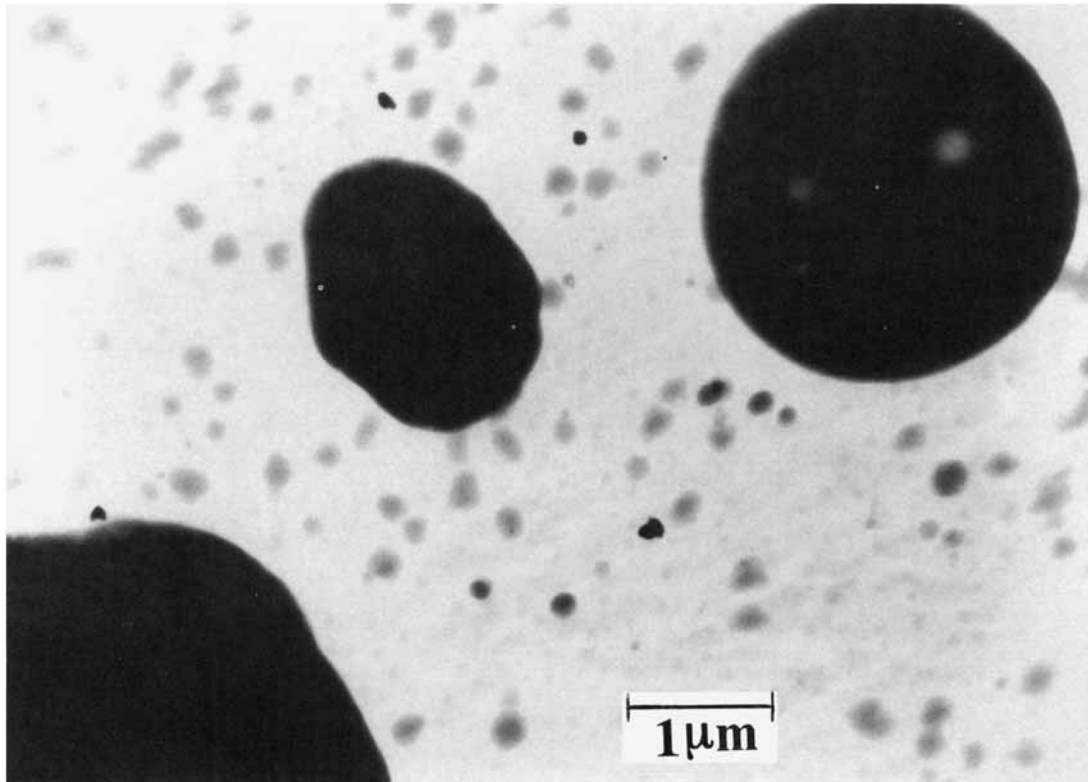
Figure 4 Plot of $\ln S_{sp}$ vs. $\ln t$ for a 50/50 nylon/HNBR dynamically vulcanized blend (0.9 phr cross-linker).

tension, and shear rate. This will be discussed in later sections. In a 50/50 dynamically vulcanized system, it is understandable from Figure 5 that the ultimate structure at 10 min mixing time is generated by breaking down of the dispersed particles under shear flow (Step C). As the particles are cross-linked and the cross-linking takes place within 1 min (cure time of pure rubber is 0.9 min determined by a curelastometer), the coalescence of particles may be assumed to be negligible. However, in the case of an uncross-linked system, the probability of coalescence is more, resulting in a larger dimension of the particles (Step F).

As the mixing is continued, the viscoelastic properties of rubber as well as the plastic are modified. For example, the viscosity of nylon decreases from 1.97×10^2 to 1.20×10^2 Pa s in 10 min shearing at 100 s^{-1} due to degradation and that of uncross-linked rubber from 2.45×10^3 to 2.20×10^3 Pa s in 7 min. The viscosity of rubber finally reaches a value of 2.39×10^3 Pa s in 10 min due to gelling. Though the viscoelastic behavior in the mixer is complex, the nature of changes should be the same. Hence, at very long mixing times (> 10 min), the highly gelled HNBR particles agglomerate and settle in a low viscous nylon matrix. As shown in Figure 3, this effect is more prominent for a dynamically vulcanized system.

Effect of Mixing Temperature

Mixing was also carried out at different temperatures (240, 250, 275, and 300°C), keeping the mixing time



Photograph 1 Transmission electron micrograph of a 50/50 dynamically vulcanized rubber/plastic blend; the black particles are rubber stained with ruthenium tetroxide (mixing time 10 min at 250°C).

(10 min) constant. The results are shown in Figure 6. The mean radius of the dispersed particles and the correlation distance increase with increasing temperature. The specific interfacial area accordingly decreases. At 300°C, \bar{R} becomes more than double and S_{sp} decreases by about 50% as compared to the values obtained after mixing at 250°C. The results may be explained from the model given in

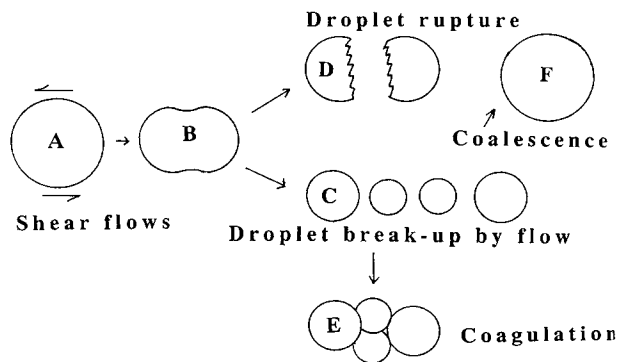


Figure 5 A model for the formation of droplets (C), droplet rupture (D), coagulation (E), and coalescence (F) of droplets.

Figure 5. The efficiency of the breakdown process, the curing reaction, and the difference in viscosity of nylon and rubber increase with the increasing mixing temperature. Ten minutes mixing time is long enough at higher temperature (as compared to that at 250°C), resulting in coagulation of the particles (Step E in Fig. 5). It is shown in Figure 3 that the agglomeration takes place after 10 min residence time at 250°C.

Effect of Degree of Cross-linking

The degree of cross-linking has been measured as the gel fraction (g). The effect of g on the structure parameters is shown in Figure 7. The average size of the dispersed particle increases from 0.31 to 0.85 μm , with an increase in g value from 0.07 to 0.19. The breakdown of the particles is inhibited with increased cross-linking. Steps B and D in Figure 5 may be visualized to explain the results. S_{sp} decreases and ξ increases with the degree of cross-linking.

Effect of Time of Addition of Peroxide

2,5-Dimethyl(*t*-butyl peroxy) hexane was added in the mix at different times at 250°C and mixing was

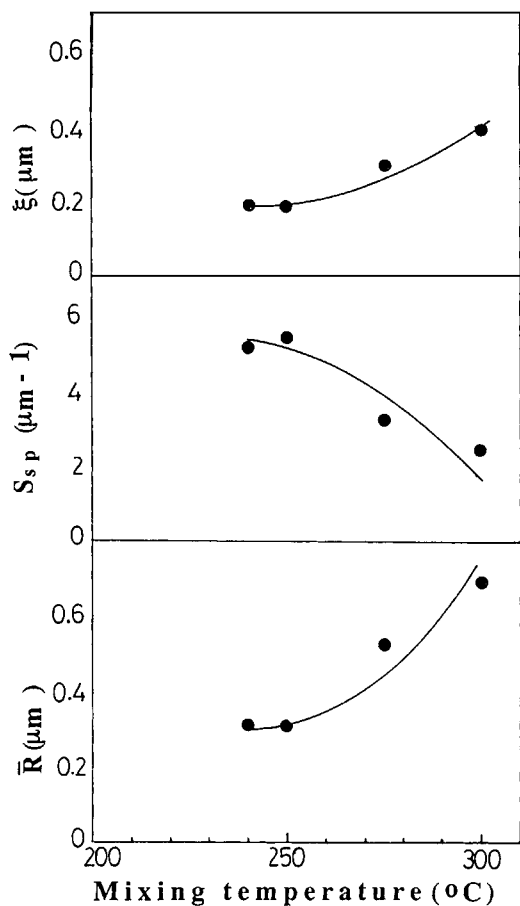


Figure 6 Effect of mixing temperature on the morphology parameters of a 50/50 nylon/HNBR dynamically vulcanized blend (mixing time = 10 min; 0.9 phr cross-linker).

continued up to 10 min. The results are shown in Figure 8. It is observed that the particles are larger when the allowed breaking down time is smaller. The correlation distance increases and the specific

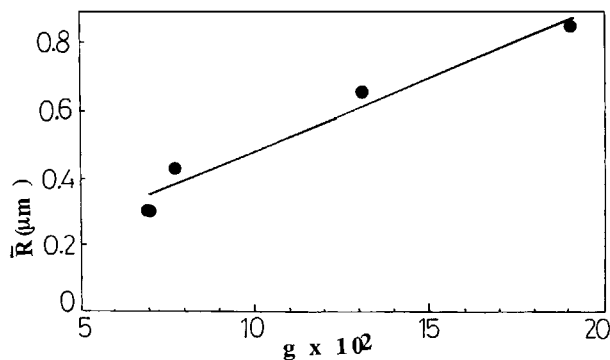


Figure 7 Effect of gel fraction on the particle size of the dispersed phase of a 50/50 nylon/HNBR system (mixing temperature = 250°C and mixing time = 10 min).

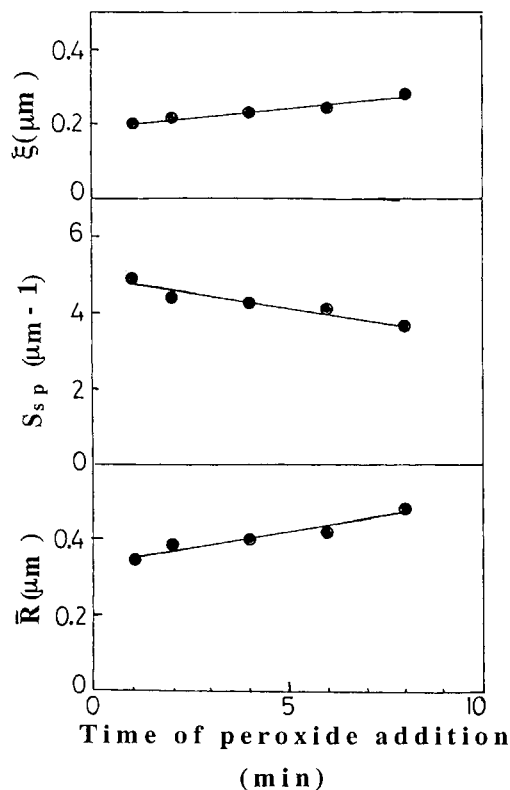


Figure 8 Effect of time of addition of peroxide on \bar{R} , S_{sp} , and ξ for a 50/50 nylon/HNBR blend mixed at 250°C.

interfacial area decreases with delayed time of addition of peroxide. A sample was taken out at 8 min mixing time just before the addition of the cross-linker. The results were compared with the system when the cross-linker was added at 8 min and the mixing continued for 10 min. The particle size (0.48 μm) does not practically change. All these observations indicate the importance of the breakdown process for structure development and the fact that the coalescence phenomenon is significant in this blend in the absence of a cross-linker.

Effect of Blend Ratio

The effect of blend ratio on structure parameters is shown in Figure 9. A 50/50 blend of both uncross-linked and cross-linked systems shows a larger particle diameter of the dispersed phase as compared to 70/30 or 30/70 rubber/plastic blends. This is further confirmed from the TEM studies. When the concentration of plastic is high, the energy supplied in the mix is absorbed by the rubber (because of the higher value of G'' ; $G''_{\text{Rubber}} = 2.32 \times 10^5$ dyne/cm² and $G''_{\text{Nylon}} = 1.90 \times 10^4$ dyne/cm² at 250°C) and utilized to break into small droplets. In the reverse case, at a high concentration of rubber in a 70/30

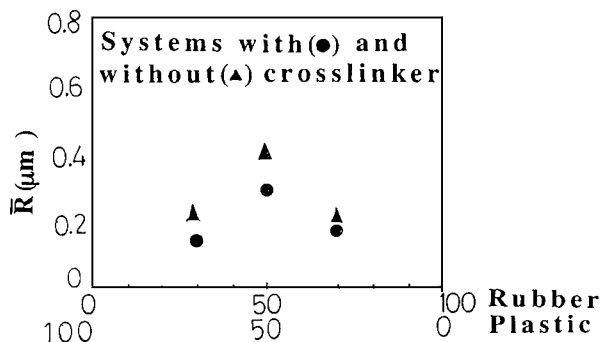


Figure 9 Particle size of the dispersed phase for various uncross-linked and cross-linked blends mixed at 250°C (mixing time = 10 min).

blend, nylon droplets become entrapped into a highly viscous rubber phase once these are broken down. At a 50/50 ratio, the net effect of these factors generates a particle size higher than those of 70/30 or 30/70 blends.

Interfacial Parameters

Figure 10 shows the time variation of interfacial thickness as measured by ellipsometry. The interface of nylon and uncross-linked HNBR is 62 nm thick at 250°C. Vulcanization of the rubber phase during the measurement reduces the thickness to 48 nm, which may be due to the restriction of the mobility of rubber chains due to cross-linking. The thickness, however, does not change with residence time even up to 30 min for both the systems. It is also interesting to note that the rubber-to-nylon interface is formed within 1 min and there is no time dependence

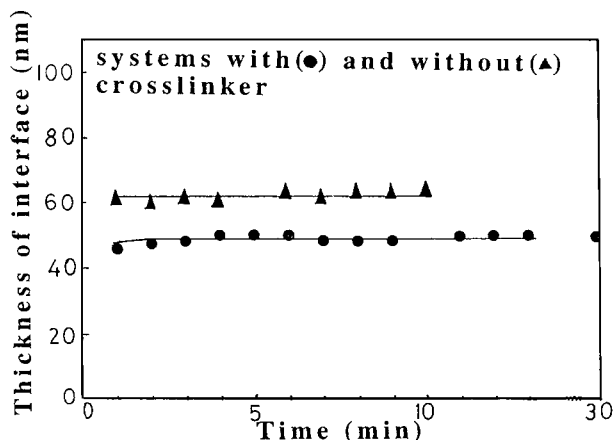


Figure 10 Time variation of interfacial thickness for uncross-linked and cross-linked (0.9 phr cross-linker) systems measured at 250°C.

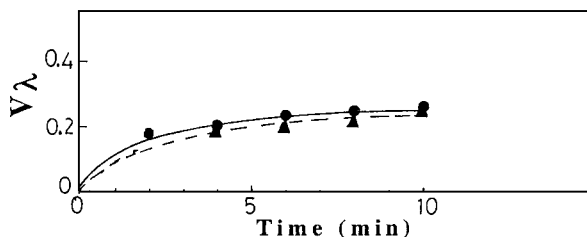


Figure 11 Plot of volume fraction of interface vs. residence time up to 10 min (mixing temperature = 250°C).

in the early stage. Multiplying the interfacial thickness with the specific interfacial area, the volume fraction of the interface (V_λ) may be calculated. Figure 11 shows such a plot. There is a marginal difference between the unvulcanized and vulcanized systems. Hence, the volume fraction of the interface created remains almost constant during mixing up to 10 min for these two systems.

To understand the small particle size of the dispersed phase in the case of a dynamically vulcanized blend, interaction parameters (χ_{PR}) and interfacial tension (γ_∞) are estimated from the interfacial thickness (λ) using the following equations¹¹:

$$\lambda = \frac{2a}{(6\chi_{PR})^{1/2}} \left\{ 1 + \ln 2 \left(\frac{1}{\chi_{PR}N_R} + \frac{1}{\chi_{PR}N_P} \right) \right\} \quad (7)$$

$$\gamma_\infty = \frac{kT}{a^2} \left(\frac{\chi_{PR}}{6} \right)^{1/2} \quad (8)$$

where a is the statistical segment length and N_R and N_P are chain lengths of the rubber and the plastic, respectively. Taking measured values of $\lambda = 48$ nm, $N_P = 90$, and $N_R = 1680$ and assuming $a = 0.8$ nm, χ_{PR} and γ_∞ are estimated to be 2.8×10^{-3} and 0.24 mN/m, respectively, at 250°C. These values are rather low considering nylon and HNBR as an immiscible system. Wu,¹⁰ however, reported a low value of interfacial tension (0.25 mN/m) for nylon and ethylene propylene rubbers. Extending Taylor's criteria to the case of viscoelastic drop in a viscoelastic matrix, Wu¹⁰ proposed a relationship between the number-average particle diameter (D) and viscosity of the dispersed phase (η_d) and the matrix (η_m), interfacial tension (γ_∞), and effective shear rate of the mixer (S_R) as follows:

$$D = 4 \cdot (\eta_d/\eta_m)^{0.84} \cdot \gamma_\infty / (S_R \cdot \eta_m) \quad \text{for } \eta_d/\eta_m > 1 \quad (9)$$

Using the measured values of viscosity of nylon and cross-linked hydrogenated nitrile rubber and γ_∞

= 0.24 mN/m, D is estimated to be 0.71 μm . Considering the assumptions and approximations, the mean radius of the dispersed particle, \bar{R} ($= D/2$), determined experimentally, is in line with the theoretical prediction. Low values of χ_{PR} and γ_{∞} and a high value of λ for the present system may be explained in the following way: During treatment at high temperature (250°C), nylon and HNBR generate free radicals because of their structural characteristics and degrade, which may be further confirmed indirectly from the viscosity values in the dynamic mechanical measurements (as reported in an earlier section). These free radicals may recombine to give graft polymers that act as an interfacial agent and reduce the interfacial tension between nylon and HNBR. The interfacial thickness, as a result, increases.

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