Influence of Dynamic Vulcanization and Phase Interaction on the Swelling Behavior of the Thermoplastic Elastomeric Blends of Nylon-6 and Acrylate Rubber in Various Solvents and Oil

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ABSTRACT: The swelling behavior of thermoplastic elastomeric blends of nylon-6 and acrylate rubber (ACM) has been studied in various solvents and oil at different temperatures. The blends, both with and without dynamic vulcanization, show excellent solvents and oil resistance at elevated temperature. The interfacial reaction between nylon-6 and ACM phases as well as the dynamic crosslinking of the ACM phase during melt blending tremendously improve the solvent resistance of the blends. A simple thermodynamic model, based on the Flory–Huggins equation, is applied to find out the constraining effect of the continuous nylon-6 matrix (which is the least swellable phase) on the extent of equilibrium swelling of the dispersed ACM phase in toluene at 25°C. The diffusion coefficients of various solvents and the activation energy of diffusion of toluene in 40 : 60 (w/w) dynamically vulcanized blend have been reported. The occurrence of interfacial reaction and the existence of nylon-6–ACM graft copolymers are also supported by the dynamic mechanical thermal analysis of the blends. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2331–2340, 1998

Key words: nylon-6; acrylate rubber; thermoplastic elastomer; swelling; diffusion coefficients

INTRODUCTION

Thermoplastic elastomers prepared from rubber/ plastic blends have gained importance in recent years.[1,2] They have the ease of processing like thermoplastics and behave like a crosslinked rubber at ambient conditions. In most cases the morphology of these blends consists of finely divided rubber particles dispersed in a relatively small amount of plastic. The rubber particles should be vulcanized or crosslinked during blending operation to promote elasticity of the materials.[1] The

rubber/plastic combinations in thermoplastic elastomers are immiscible in nature and technological compatibilization of the immiscible pairs is necessary in order to improve the mechanical properties of the blends for commercial uses. Technological compatibilization of various thermoplastic elastomeric rubber/plastic blends has been discussed earlier.[3–5]

Preparation and the properties of the thermoplastic elastomers from reactive blends of nylon-6 and acrylate rubber (ACM) has been reported recently,[6] where the amine or the carboxyl end groups of nylon-6 react with the reactive epoxy groups of ACM to produce the necessary graft copolymer at the interface during melt blending, which in turn compatibilizes the two component phases. In this article the influence of dynamic

vulcanization and the interfacial reaction on the solvent and oil resistance of the blends is high-lighted. Using this knowledge, our aim is to develop a thermoplastic elastomer with improved heat and oil-resistance properties. Coran and Patel[7] reported the properties of heat and oil-resistant thermoplastic elastomers from polyamides/chlorinated polyethylene (CPE) reactive blends. Saltman and Varnell[8] reported a pseudoblock copolymer prepared by grafting *in situ* nylon-acrylic rubber with proprietary grafting technology. The grafting results in a dramatic reduction in oil swell in ASTM oil #3 and a substantial improvement of the retention of tensile strength at 150°C.

Swelling measurement is a useful method for phase studies in polymer blends. The extent of swelling in a particular solvent is expected to be sensitive to changes in the structure of the component polymer phases and can be related to the properties of the polymer chains such as molecular mobility, phase interaction, and so on. In this article the focus of our work is an investigation of the swelling behavior of nylon-6/ACM reactive blends in different solvents, ASTM fuels, and oil and to correlate the swelling characteristics to the structural and morphological changes associated with the chemical reaction at the interface and vulcanization of the rubber phase. Thermodynamic model of swelling of heterogeneous polymeric networks has been reported by several authors.[9–11] Coran, Patel, and Williams[12] discussed the swelling behavior of thermoplastic vulcanizates by using model PP/EPDM composition and studied the effect of rubber/plastic proportions and the extent of vulcanization on the volume swell of the blends in different solvents and ASTM oil.

EXPERIMENTAL

Materials

Nylon-6 (Ultramid B3) in pellet form [viscosity number = 150 mL/g (0.005 g/mL sulfuric acid solution)] was supplied by BASF, Germany. Acrylate rubber (ACM), NIPOL AR51 (sp. gr. = 1.1 at 25°C) was obtained from Nippon Zeon Co. Ltd., Tokyo, Japan. It is reported to have epoxy cure site and made from ethyl acrylate monomer. Hexamethylene diamine carbamate, DIAK #1 (Du Pont), was supplied by NICCO Corporation Ltd., India. Immersion fluids for the swelling tests were n-hexane ($\delta = 14.9$), carbon tetrachloride ($\delta = 17.6$), xylene ($\delta = 18.0$), toluene ($\delta = 18.2$),

benzene ($\delta = 18.8$), methylethylketone ($\delta = 19.0$), chloroform ($\delta = 19.0$), cyclohexanone ($\delta = 20.3$), nitrobenzene ($\delta = 20.5$), n-butanol ($\delta = 23.2$), and dimethylsulfoxide ($\delta = 24.6$). The values in the parentheses indicate solubility parameter, δ, in MPa$^{1/2}$. Toluene and iso-octane at different volume ratios were mixed to prepare ASTM fuels (e.g., A, B, C, and D). For oil resistance testing, ASTM oil #3, supplied by APAR Ltd., India, was taken. The solubility parameters of the liquids were taken from the Polymer Handbook.[13]

Preparation of Thermoplastic Elastomeric Composition

Nylon-6 and ACM were dried at 100°C for 24 h *in vacuo* prior to blending. The blends were prepared in batches of 50 g polymer in a Brabender Plasticorder (PL 2000-3) mixer with roller type rotor at a mixer set point temperature of 220°C. The rotor speed was kept at 40 rpm. Nylon-6 was first charged and melted for 2 min. After the nylon had melted, ACM was added and mixed for different times under the same conditions. The change of mixing torque with mixing time along with the stock temperature was recorded for each blend. As the mixing continued, the stock temperature gradually rose to 235°C and the torque value showed an upward trend, indicating the interfacial reaction between nylon-6 and ACM. After a specified time of mixing the resulting blend was quickly removed from the mixer and passed through the close nip-gap of a water cooled two-roll mill to stop the reaction. A similar procedure was followed for all the blends. The blend samples, which showed thermoplastic elastomeric behavior, were also subjected to dynamic vulcanization. In this processing stage, hexamethylenediaminecarbamate (HMDC) was added after 8 min of mixing. The mixing was continued for another 5 min after HMDC addition and the blends were treated as before. The formulations and the mixing details of the mixes are given in Table I.

Molding of Thermoplastic Elastomer

Test specimens ($\sim$ 1.2 mm thick) were prepared in a Moore press by compression molding at 230°C in a frame-and-plate mold between two well released aluminum foils for 2 min for all the samples and immediately cooled by passing water under pressure. The samples were removed from the mold when the temperature came down to 100°C.

Table I Formulations of Mixes

Composition Number	Nylon-6	ACM	DIAK #1, phr.	Mixing Time (min)	Comments
1	40[a]	60[a]	—	13	Variation of rubber-plastic ratio
2	45	55	—	13	
3	50	50	—	13	
4	55	45	—	13	
5	60	40	—	13	
6	40	60	0.5[b]	13	Variation of rubber-plastic ratio
7	45	55	0.5	13	(dynamic vulcanization)
8	50	50	0.5	13	
9	55	45	0.5	13	
10	60	40	0.5	13	
11	40	60	0.25	13	Variation of crosslinking
12	40	60	0.75	13	density
13	40	60	1.00	13	
14	40	60	—	3	Variation of mixing time
15	40	60	—	5	(extent of phase interaction)
16	40	60	—	7	
17	40	60	—	9	
18	40	60	—	11	
19	100	—	—	13	Pure components
20	—	100	0.5	Mill mixing and cure at 220°C for 7 min	

[a] Weight percent.
[b] 0.5 g/100 g rubber.

Dynamic Mechanical Analysis

Dynamic mechanical thermal analysis of the blends and the component polymers were performed on a DMTA Rheometric Scientific MK-II model in bending dual cantilever mode. The experiments were carried out at a frequency of 10 Hz, at a heating rate of 2°C/min and a double strain amplitude of 64 μm over a temperature range of -100°C to 150°C. The data were analyzed by a COMPAQ Computer and storage modulus, E', loss modulus, E'', and loss tangent, tan δ, were measured for each sample in this temperature range.

Swelling Test

Circular test pieces of radius of $\sim$ 20 mm were die cut from the molded sheets (1.2–1.5 mm thick). These were weighed accurately and immersed in the solvents at room temperature (25°C). After specified time of swelling, the specimens were removed from the solvents, blotted and weighed in a glass-stoppered bottle. Also, the thickness of the swollen samples were measured simultaneously. Volume swelling for a specimen was estimated as

$$q - 1 = (W_2/W_1 - 1)\rho_c/\rho_s \qquad (1)$$

where q is the ratio of swollen volume to original unswollen volume ($q - 1$ = % of volume swell $\div$ 100), W_1 and W_2 are specimen weights before and after swelling, respectively, ρ_c and ρ_s are the density of the composition and the solvent, respectively. Swelling studies were performed also at 40°C and 50°C in toluene. Hot oil swelling was determined in ASTM oil #3 at 150°C after 72 h according to ASTM D471-93. The density of the specimens (blends) was taken as 1.12 g/cc (average value). The densities of the solvents and the mixture of the solvents were taken from the standard handbook. The density of the ASTM oil #3 at 150°C measured using the standard procedure was 0.86 g/cc.

Diffusion coefficients of the solvents at room temperature and at higher temperatures were calculated from the measurements of swelling of the blends as a function of time:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2}$$

$$\times \exp\left[-(2n+1)^2\pi^2\frac{Dt}{l^2}\right] \quad (2)$$

where M_t is weight fraction of the solvent absorbed at time t and M_∞ is the weight fraction of the solvent at equilibrium, that is, as t approaches infinity. Here D is the diffusion coefficient of the solvent and l the thickness of the sample at time t. The corresponding solution useful for small times is[14]

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{l^2}\right)^{1/2}\left[\pi^{-1/2}\right.$$

$$\left. + 2\sum_{n=1}^{\infty}(-1)^n \text{ ierfc }\frac{nl}{(Dt)^{1/2}}\right] \quad (3)$$

which could then be simplified to

$$\frac{M_t}{M_\infty} = 2\left[\frac{Dt}{\pi l^2}\right]^{1/2} \quad (4)$$

As the thickness of the blend samples used in the experiment changed during swelling, M_t/M_∞ was plotted against $\sqrt{t}/l$ to consider the thickness change. From the slope of the curve, the diffusion coefficient of the solvents was measured.

The activation energy of diffusion was determined from the temperature dependence of diffusion, which can be expressed by an Arrhenius-type expression:

$$D = D_o \exp(-E_D/RT) \quad (5)$$

where D_o is the frequency factor, E_D the energy of activation for diffusion, R the universal gas constant, and T the absolute temperature.

RESULTS AND DISCUSSION

Swelling Behavior in Various Solvents at 25°C

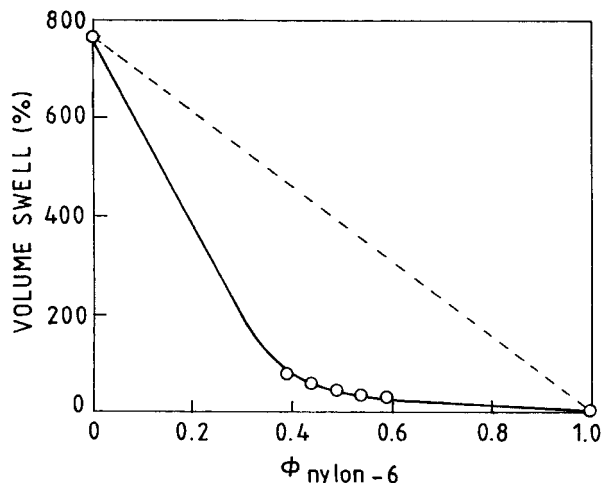#### Influence of Dynamic Vulcanization

Figure 1 shows the swelling data of the 40 : 60 nylon-6/ACM (w/w) blends (with and without dynamic vulcanization) in different solvents at room temperature. Volume swelling percent has been
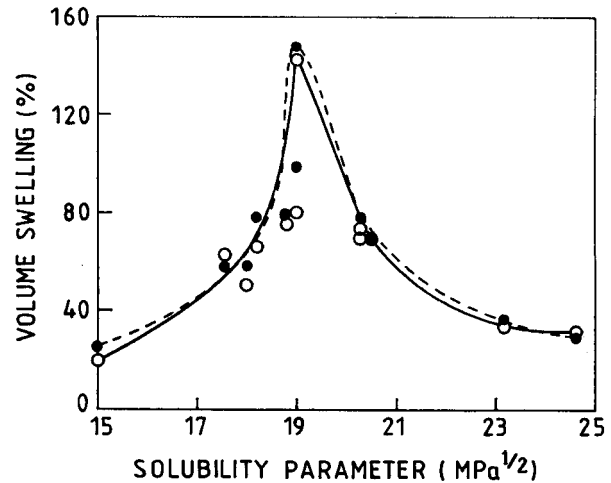
Figure 1 Equilibrium volume swell (%) of 40 : 60 nylon-6/ACM (w/w) blends versus solubility parameter of the solvents at 25°C ($\bullet$), without dynamic vulcanization and ($\bigcirc$) with dynamic vulcanization.

plotted as a function of the solubility parameter of the solvents. The curve shows a maxima around 19 $(MPa)^{1/2}$ which is very close to the solubility parameter of the acrylate rubber: 18.7 $(MPa)^{1/2}$. As nylon-6 is a highly crystalline material and its crystallinity is retained to some extent in the blend with ACM, the above result suggests that the swelling of the ACM phase is of more importance in controlling the overall swelling behavior of the blends. The value at which the peak in volume swelling occurs is also independent of dynamic vulcanization.
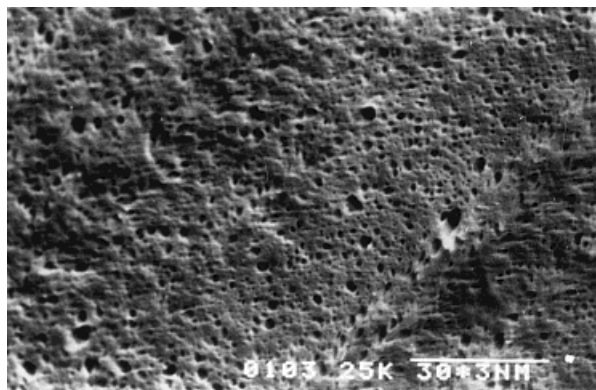
Figure 2 shows the volume swelling data of the nylon-6/ACM blends (without dynamic vulcanization), swollen by toluene at room temperature as a function of the volume fraction of the hard phase, that is, nylon-6. The dashed line connecting the two ends represents the average swelling characteristics of the hypothetical blends of nylon-6 and ACM having no morphological or structural constraints present in the system. The shape of the experimental curve definitely indicates extreme constraint on the equilibrium swelling of the ACM present in the blend system. As pure nylon-6 swells to an insignificant extent in toluene at room temperature, the above said constraint suggests the formation of the nylon-6 as the continuous matrix which restricts the swelling of the dispersed ACM phase in it. The SEM photographs of the blends also support the above morphology, as shown in Figure 3, for the representative 50 : 50 (w/w) nylon-6/ACM blend, where ACM particles of $0.5-1$ μm dimensions are
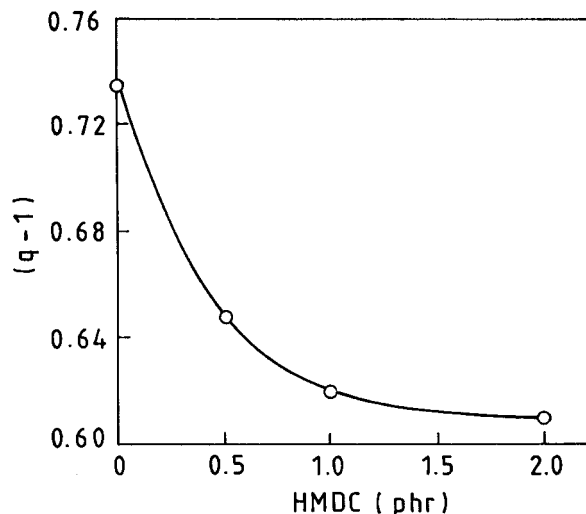
Figure 2 Equilibrium volume swell (%) of nylon-6/ACM blends in toluene at 25°C versus volume fraction of nylon-6.

Figure 4 Equilibrium volume swelling (%) versus concentration of HMDC in ACM for 40 : 60 nylon-6/ACM (w/w) blend swollen by toluene at 25°C.

found to be dispersed in continuous nylon-6 matrix.

Figure 4 describes the effect of dynamic vulcanization of the rubber phase on volume swelling in toluene at room temperature for 40 : 60 (w/w) blend. Though the continuous nylon-6 phase as well as the grafting reaction (discussed later) greatly constrain the swelling of the rubber phase, the effect of vulcanization is quite large. It is found that with increasing curative level, the volume swell decreases sharply and then attains an equilibrium value. Further addition of the curing agent does not alter the crosslinking density of the

Figure 3 Scanning electron micrograph, examined by Hitachi (model no. S415A) electron microscope of cryo-fractured nylon-6/ACM, 50 : 50 (w/w) blend after extracting the ACM phase by chloroform, followed by sputter-coating with gold. Note the presence of ACM as dispersed phase of dimension 0.5−1 μm in the matrix of nylon-6.

rubber phase and hence the equilibrium swelling reaches a constant value.

It is known that the equilibrium volume swelling of a lightly crosslinked homogeneous polymeric network in any solvent depends upon the interaction parameter (χ) between the solvent and the polymer and the crosslinking density of the network. The extent of equilibrium swelling can be described by the well known simplest form of the Flory−Huggins[15] equation which can be represented approximately as

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + \rho \frac{V_1}{M_c} v_2^{1/3} = 0 \quad (6)$$

where v_2 is the volume fraction of the rubber in the swollen gel, ρ is the density of the material, V_1 the molar volume of the solvent, and M_c is the molecular weight between the crosslinks. When the same polymer (in this case ACM phase) is embedded in the least swellable matrix like nylon-6, it swells against the compressive force exerted by the matrix. The situation is equivalent to the restricted swelling of the rubber phase under a hydrostatic pressure p', the extent of swelling of which can be given by

$$\ln(1 - v_2') + v_2' + \chi v_2'^2$$

$$+ \rho \frac{V_1}{M_c} v_2'^{1/3} + p^1 \frac{v_1}{RT} = 0 \quad (7)$$

Here, v_2' represents the volume fraction of the rubber in the swollen vulcanizates under the constrained swelling condition. If we replace p' by an equivalent quantity G, the shear modulus of nylon-6 phase, the above equation will give an approximate idea of the volume swelling of the ACM phase under the constraining effect of the continuous nylon-6 matrix. Putting the value of M_c from eq. (6) into eq. (7), we get

$$\ln(1 - v_2') + v_2' + \chi v_2'^2 - \left(\frac{v_2'}{v_2}\right)^{1/3}[\ln(1 - v_2)$$

$$+ v_2 + \chi v_2^2] + \frac{GV_1}{RT} = 0 \quad (8)$$

Now, taking $v_2 = 0.113$ and $V_1 = 106.3$ cc/mol, $\chi = 0.344$, $G = 2100$ MPa and solving the above equation for nylon-6/ACM system, the value of v_2' is obtained as 0.506 when the curative level of HMDC in ACM is 0.5 phr. This is equivalent to a volume swell percentage of 97.6% of ACM in the blend having nylon-6 as the main matrix. The original free swelling volume of the acrylate rubber (crosslinked to the same extent) in toluene at room temperature is 786%. The above calculation presupposes that the shear modulus of the nylon-6 matrix remains unchanged in the blends (in reality the modulus value depends upon the percent crystallinity of the polymer and the latter is changed in the blends)[16] and also that the crosslinking density of ACM phase remains the same in the blends compared to that found in the pure sample (this is an oversimplified assumption as the crosslink density of the ACM phase in the above two cases may be different due to different heat histories of the samples during processing: static and dynamic vulcanization).

Figure 5 shows both the calculated and the experimental volume swell percentage of the blends versus the volume fraction of the hard phase present in the blends. It is clear from the figure that above a certain volume fraction of nylon-6, the volume swelling of the blends is still much lower than the corresponding predicted theoretical values, the difference between the two increases with increasing plastic content. This behavior clearly suggests that apart from the restriction of the swelling of the ACM particles by nylon-6 matrix alone, there are other factors which further impose constraint on the swelling of the ACM phase. This additional restriction may come from (1) good adhesion between nylon-6 and ACM at their
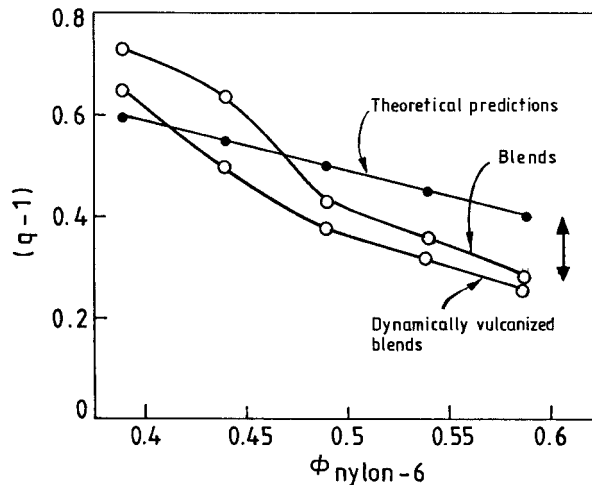
Figure 5 Equilibrium volume swell (%) of nylon-6/ACM blends in toluene at 25°C versus volume fraction of nylon-6.

interface, which is believed to be achieved by the grafting reaction between the two during melt-blending operation. The flexibility of the ACM rubber chains when grafted to the plastic matrix is expected to be greatly reduced relative to that of the chains in the bulk polymer, with the mobility increasing gradually with increasing distance from the boundary. Thus, a layer of restricted chain mobility is formed near the phase boundaries and due to higher stiffness of the ACM chains in this layer, this zone swells to a lesser extent than that of the bulk rubber zone. (2) Increased thickness of the nylon separating the acrylate rubber or smaller dimension of the rubber particles, (3) increased crystallinity with increasing nylon-6 content, and (4) occlusion of rubber particles by nylon.

There is another important point to note in Figure 5, which shows that 40 : 60 (w/w) blend swells to a greater extent than that predicted from the theoretical calculation. In the case of the blends with higher rubber content, there is a probability of formation of an interlinked rubber network after certain percentage of swelling, as in those cases the interparticle distance is low before swelling and the distance is further decreased due to expansion of the rubber network during swelling. This ultimately leads to the formation of a co-continuous phase morphology or, in other words, this destroys the continuity of the nylon-6 matrix and hence the restriction imposed on the swelling of the ACM phase by it is removed. Thus, the 40 : 60 (w/w) nylon-6/ACM blend shows

higher percentage of swelling than that of the predicted value.

Influence of Interaction

In order to study the effect of interaction on the swelling behavior of the blends, the mixing was carried out to different extents (i.e., for different times) for 40 : 60 (w/w) blend and the molded samples were swollen in toluene under the identical conditions stated in the Experimental section. Figure 6 summarizes the time dependence of the volume swelling of the blends at room temperature. It is clear from the figure that both the extent of equilibrium volume swelling and the initial rate of swelling decrease progressively with increasing reaction time, that is, with increasing the extent of the interfacial reaction. Since the volume fraction of ACM in these blends is constant, the above results can be interpreted by assuming that as the level of grafting between nylon-6 and ACM increases with increasing reaction time, the relative volume of the "restricted mobility zone," as discussed earlier, increases, resulting in more restricted swelling and hence lower volume swelling percentage. For the sample with lowest interaction (i.e., with 5 min of reaction), the swelling of the rubber phase is high, which results in the disintegration of the blend sample (shown by the dashed line) due to excessive stress build-up at the interface during swelling.
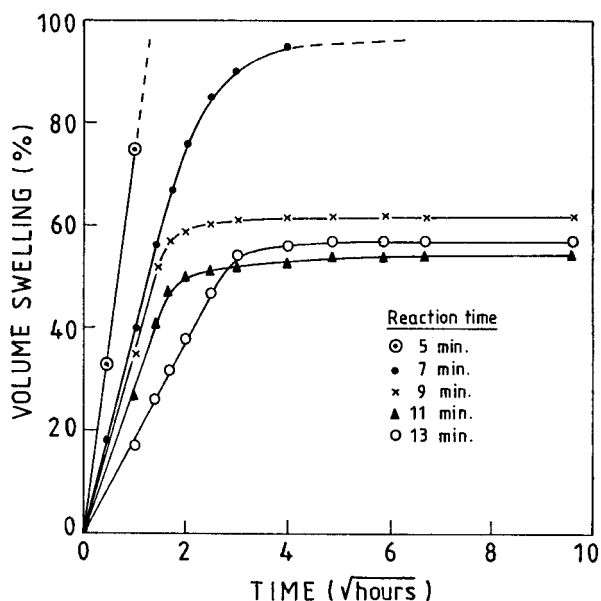

Figure 6 Time dependence of volume swelling (%) of 40 : 60 blends interacted for different times in toluene at 25°C.

The existence of a restricted mobility zone in the dispersed ACM phase is also supported by dynamic mechanical thermal analysis of the blends. Figure 7 shows the DMTA results of pure ACM, nylon-6, and 50 : 50 (w/w) blend of nylon-6 and ACM in terms of temperature dependence of tan δ in the temperature range between $-100°C$ to 150°C. The glass-transition temperature (T_g) of ACM and nylon-6 are found at 0°C and 98°C, respectively, besides other secondary transitions. The 50 : 50 (w/w) nylon-6/ACM blend shows two peaks, one at $-2.5°C$ corresponding to the T_g of ACM and another broad peak at 85°C due to the T_g of nylon-6. Apart from that, a secondary damping peak is observed at 14°C, at the slightly higher temperature side of the T_g of the ACM phase, the appearance of which strongly suggests the formation of "restricted mobility zone" in the ACM phase during the reactive blending operation. In the case of 40 : 60 (w/w) blend with different interaction, the above feature is also observed as the secondary tan δ peak appears gradually at higher temperature region with increasing level of interaction (Fig. 8). In the blends with 9 and 11 min of reaction, it appears as a shoulder at 13°C and 17°C, respectively; but after 13 min, a distinct secondary peak is observed at 22.5°C.
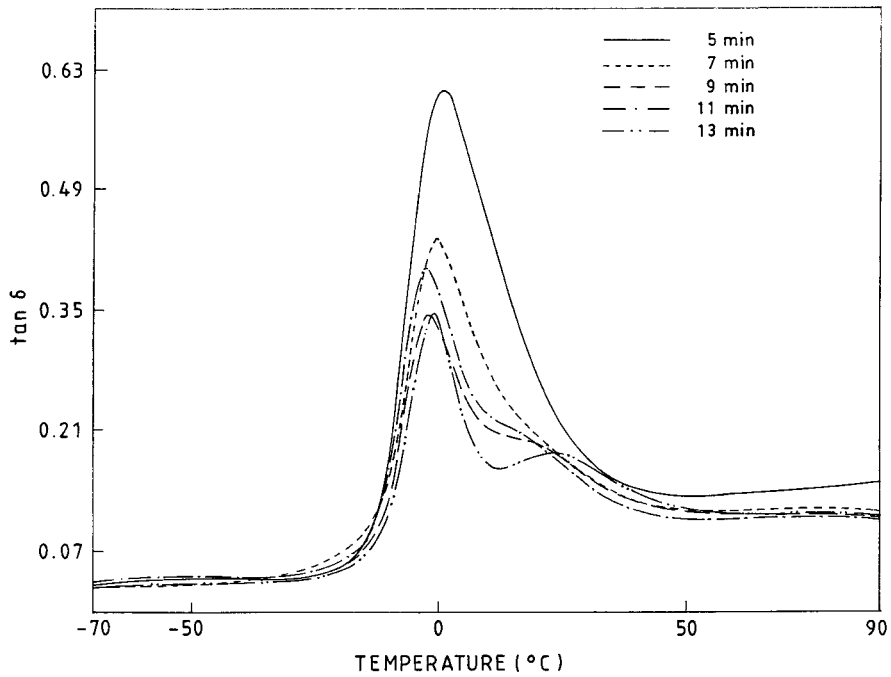
Diffusion Coefficients

The diffusion coefficients, calculated by using eq. (4), of various solvents for dynamically vulcanized 40 : 60 nylon-6/ACM (w/w) blend at 25°C are shown in Figure 9, as a function of the solubility parameter of the solvents. The solvents are arranged according to the increasing solubility parameter. Though the equilibrium swelling of the polymeric network in any solvent is a thermodynamic phenomenon and the diffusion coefficient of the solvent is a kinetic parameter, the two often result in the same conclusion about the nature of the polymer itself. This is manifested in the above results. Like the swelling test, the diffusion coefficient also shows maxima at the solubility parameter 18 $(MPa)^{1/2}$, which is close to that of the acrylate rubber: 18.7 $(MPa)^{1/2}$. Moreover, the above results indicate that for the above blend system, the diffusion coefficient depends on the interaction between the rubber and the liquid, rather than on the viscosity of the liquid. Figure 10 represents the variation of diffusion coefficient of toluene in nylon-6/ACM blends at 25°C with the weight fraction of the rubber phase in the blend. Similar to the volume swelling data, the $\bar{D}$
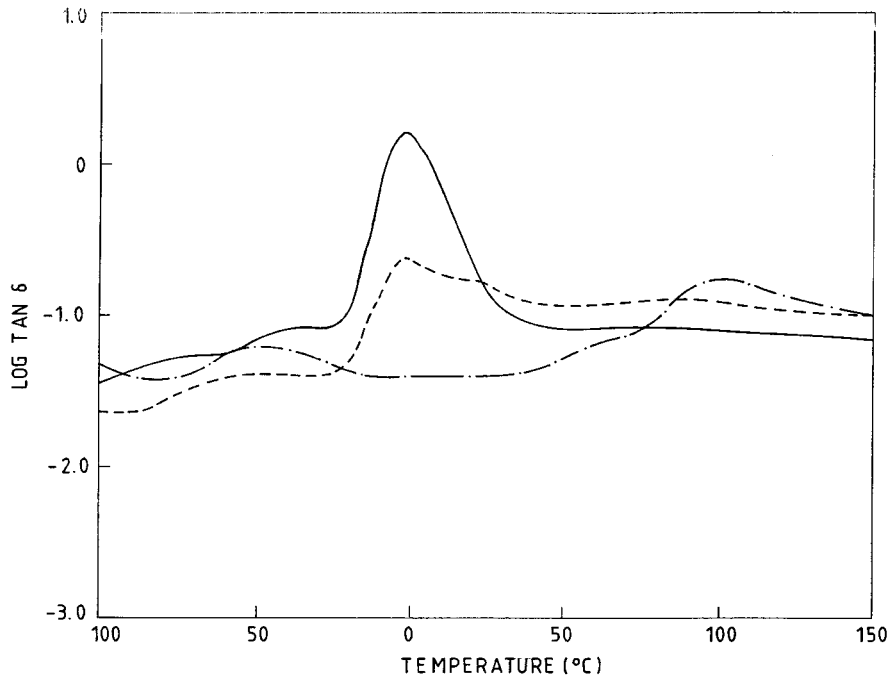
Figure 7 Temperature dependence of loss tangent (tan δ) of nylon-6 ($- \cdot - \cdot -$), ACM (——) and 50 : 50 nylon-6/ACM blend (-------).

value decreases with increasing plastic (i.e., nylon-6) content and the dynamically vulcanized blends show lower $\bar{D}$ values compared to those of the blends without dynamic vulcanization. In the case of 40 : 60 nylon-6/ACM (w/w) dynamically vulcanized blend, swollen by toluene, the activa-


Figure 8 Temperature dependence of tan δ of nylon-6/ACM (40 : 60) blend interacted for different times.
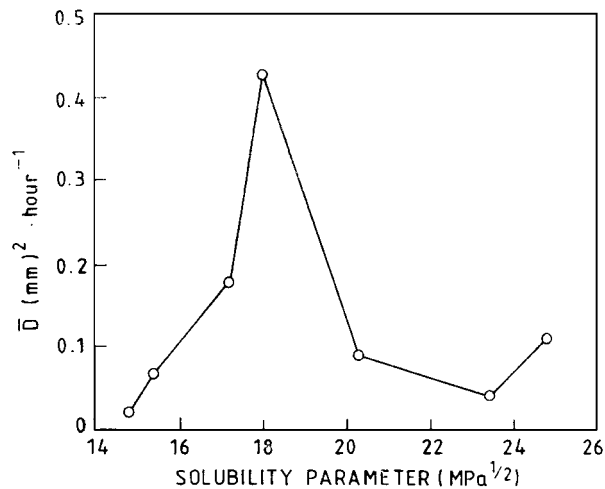
Figure 9 Diffusion coefficient (average) of various solvents for dynamically vulcanized 40 : 60 nylon-6/ACM (w/w) blend at 25°C versus solubility parameter of the solvents.

tion energy of diffusion was calculated as 45 kJ/mole. The values of E_D for octadecane, octadecanol, and octadecyl stearate in pale crepe hevea rubber and other unsaturated hydrocarbon polymers fall in the range 33–38 kJ/mole.[17] The high value of activation energy also denotes the resistance of the above blends in toluene.
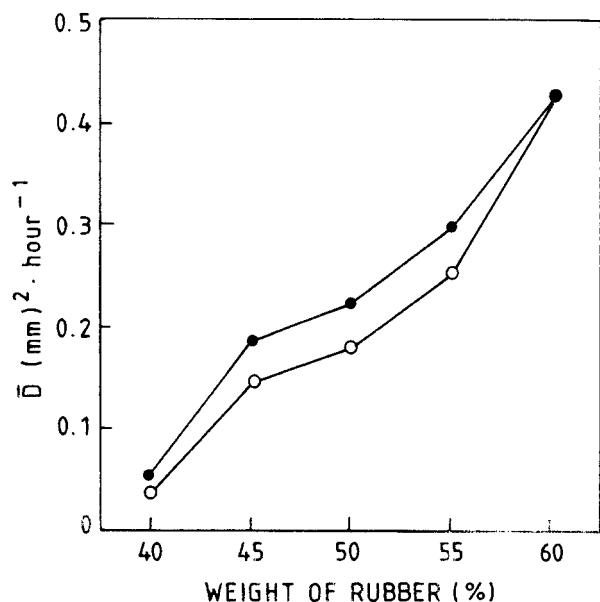

Figure 10 Diffusion coefficients (average) of toluene in nylon-6/ACM blend at 25°C versus weight fraction of the rubber phase. (●), without dynamic vulcanization; (○), with dynamic vulcanization.
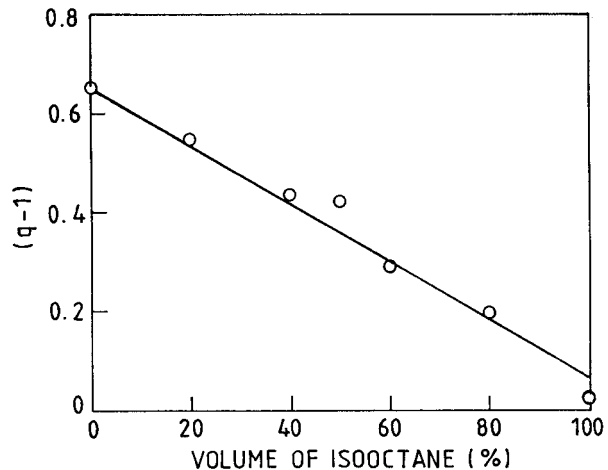
Figure 11 Equilibrium volume swelling of 40 : 60 (w/w) dynamically vulcanized blends in toluene/iso-octane mixture at 25°C versus volume percentage of iso-octane in the mix.

Swelling Behavior in Commercial ASTM Fuel and ASTM Oil

Figure 11 shows the swelling behavior of the dynamically vulcanized 40 : 60 (w/w) nylon-6/ACM blend in iso-octane/toluene mixtures at 25°C. The results signify the resistance of the blends in gasoline based fuels (ASTM fuels A, B, C, and D). Similarly, the oil resistance of the blends with various rubber/plastic ratio (dynamically vulcanized) in ASTM oil #3 at 150°C is shown in Figure 12. As expected, the volume swell decreases with
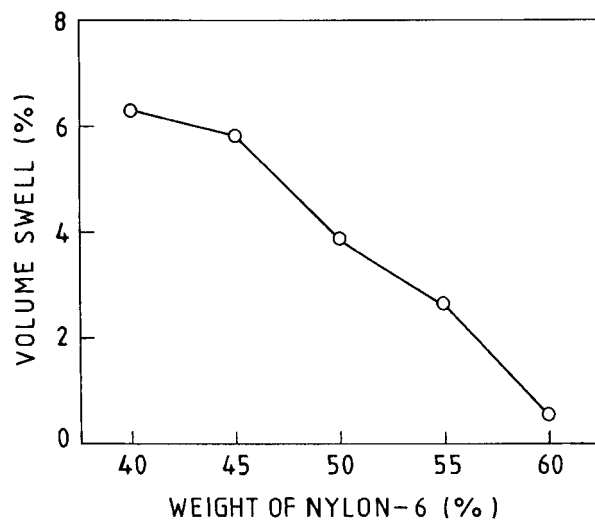
Figure 12 Equilibrium volume swelling of dynamically vulcanized nylon-6/ACM blends in ASTM oil #3 at 150°C versus weight fraction of the nylon-6 phase in the blends.

increasing plastic content in the blend. However, it is clear from both the data that the thermoplastic elastomers prepared from the blends of nylon-6 and ACM have excellent fuel and hot oil resistance. Coran and Patel[18] reported a volume swell of 22% at 100°C in ASTM oil #3 for NBR/PP (50 : 50) thermoplastic vulcanizate, whereas the 40 : 60 (w/w) dynamically vulcanized nylon-6/ ACM blend swells only 6% by volume in ASTM oil #3 at 150°C.

CONCLUSIONS

The swelling behavior of nylon-6/acrylate rubber blends in various solvents and oil has been studied and the effect of blend ratio, dynamic cross-linking of the ACM phase, and the extent of interaction between the two phases on the extent of swelling have been examined. The swelling of the dispersed ACM particles in nylon-6 matrix is greatly constrained compared to that of the free swelling of crosslinked ACM rubber in the same solvent. This is due to the constraints imposed by the least swellable continuous phase (i.e., hard nylon-6 matrix) and also due to the formation of a reduced mobility zone in the ACM phase by grafting reaction at the interface. To evaluate the constraints imposed by the nylon-6 matrix alone, a simple thermodynamic model based on the modified Flory–Huggins equation has been applied to this system. The negative deviation of the experimental volume swelling data compared to those predicted by the theoretical model is attributed to the interfacial reaction between nylon-6 and ACM during the melt blending/molding operation. With increasing the extent of the reaction between the two phases, both the rate of swelling and the equilibrium volume swelling of 40 : 60 (w/w) blend decrease progressively. Also, the increase in the crosslink density of the rubber phase substantially improves the solvent resistance of the blends. The fuel resistance of 40 : 60 (w/w) nylon-6/ACM (dynamically vulcanized) blend at 25°C and oil resistance (in ASTM oil #3) at 150°C are found to be excellent.

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