

Effect of Fillers and Plasticizers on the Performance of Novel Heat and Oil-Resistant Thermoplastic Elastomers from Nylon-6 and Acrylate Rubber Blends

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ABSTRACT: The effects of various fillers (SRF black, silica, and clay) and plasticizers (dibutyl phthalate and dioctyl phthalate) on the mechanical, dynamic mechanical, and rheological properties and on the heat and oil resistance of the thermoplastic elastomeric reactive blends of nylon-6 and acrylate rubber (ACM) were investigated. The mixing torque behavior of the blends in Brabender Plasticorder shows reduced extent of interaction between the two component polymers in the presence of both fillers and plasticizers. Silica-filled blends show the highest viscosity increment due to the possibility of reaction between its surface silanol groups and the reactive epoxy groups present in the ACM chain during melt-blending operation. Though the addition of fillers reduces the processability of the blends, it improves the extensibility as well as the tension set properties of the blends. The mechanical integrity and the damping characteristics of the blends are also improved with the addition of fillers; the latter is evidenced from the dynamic mechanical thermal analysis of the blends. The tensile strength and hardness of the filled blends remain practically unchanged after ageing at 175°C for 72 h and, also, the oil swell does not change appreciably with the addition of fillers. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1490–1501, 1999

Key words: nylon-6; acrylate rubber; thermoplastic elastomer; rubber; blends; fillers; plasticizers; heat and oil resistance

INTRODUCTION

Thermoplastic elastomers prepared from rubber–plastic blends have gained considerable interests in recent years.^{1–3} They offer the simplest route to achieve outstanding properties at low cost. A wide range of properties can be tailor-made by simple means like variation of the blend ratio, the viscosity of the components, and incorporation of suitable additives, fillers, processing aids, and

crosslinking agents. Hence, it can provide a wide variety of performances to meet diverse industrial applications in a cost-effective way. Several researchers reported on the thermoplastic elastomeric rubber–plastic blends. The first useful rubber–plastic blends were those from nitrile rubber (NBR) and poly(vinyl chloride) (PVC).⁴ The polyolefinic blends, comprised of polypropylene (PP) and ethylene propylene diene rubber (EPDM), were introduced commercially in 1972.^{5,6} Coran⁷ reported several aspects of these rubber–plastic blends, namely, the thermodynamics, physical properties, morphology, and crosslinking of rubber phase during mixing (dynamic vulcanization). The thermoplastic elastomeric natural rubber (NR) and PP blend has been discussed by Elliott.⁸ Recently, we have reported the development and

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properties of novel heat and oil-resistant thermoplastic elastomers from the reactive blends of nylon-6 and acrylate rubber (ACM).⁹ The influence of chemical interaction between the components on the mechanical, dynamic mechanical, rheological, and oil/fuel resistance of the blends have been discussed.^{9–11} In this article, the effect of various fillers and plasticizers on the ultimate properties of the above blends has been highlighted.

It is well known that addition of fillers to polymers (rubber or plastic) is an attractive way to improve several physical properties of the polymers. Apart from the considerable cost reduction of the ultimate products, fillers form an integral part of the compounding ingredients of polymers. However, the addition of fillers can be detrimental to several key properties of rubber–plastic blends; and, thus, its use in thermoplastic elastomeric rubber–plastic blends is restricted, as evidenced from the literature.^{2,12} As the hard plastic phase provides the reinforcement to the blends, addition of reinforcing fillers is often not necessary. It is observed by Rader² that carbon-black fillers, as a rule, cannot provide reinforcement in PP–EPDM thermoplastic elastomers, as opposed to traditionally cured EPDM rubber formulations. Coran¹² reported that addition of small amount of clay in nylon-6–NBR thermoplastic elastomeric blends have little effect on hardness, stiffness, or strength, though extensibility is reduced. Also, the effect of fillers on thermoplasticity is severe; and, in order to obtain the full benefit of filler usage, plasticizers can be used to regain both thermoplasticity and extensibility. Akhtar et al.¹³ reported the processing behavior and dynamic mechanical properties of filled and unfilled thermoplastic elastomeric NR–PE blends. In spite of the above facts, the studies regarding the effect of fillers (SRF black, silica, and clay) and plasticizers on various key properties of nylon-6–ACM blends have been undertaken by us due to several reasons, as follows.

1. The ACM rubber used in the study has very poor green strength with low extensibility. Addition of fillers can improve the above properties of the ACM phase and hence those of the blends.
2. The filled ACM phase would show greater resistance to swelling in oils at high temperature compared to the unfilled one; hence, the overall hot-oil resistance of the blends can be improved.
3. It will reduce the cost. Moreover, the nylon-

6–ACM blends being reactive in nature, it would be interesting to study its behavior in the presence of fillers and plasticizers.

EXPERIMENTAL

Materials

Nylon-6 (Ultramid B3) in pellet form [viscosity number = 150 mL/g (solution: 0.005 g/mL, sulphuric acid)] 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 was reported to have epoxy cure site and made from ethyl acrylate monomer. Hexamethylene diamine carbamate (HMDC) DIAK#1 (Du Pont) used as a crosslinking for acrylate rubber was supplied by NICCO Corporation Ltd., India. The silica used was Ultrasil VN₃, manufactured by Degussa, Germany, and its characteristics were as follows: surface area, 234 m²g⁻¹; oil absorption, 240 g per 100 g; pH 6. The SRF carbon black, N770, (DBP absorption, 70 cc per 100 g) was obtained from Phillips Carbon Black Ltd., Durgapur, India. China clay (specific gravity = 2.6) was obtained from Bata India Limited, Batanagar, India. Dibutyl phthalate (DBP) and Dioctyl phthalate (DOP) used in this work were of laboratory reagent grade.

Preparation of Blends

The formulations of the different mixes are given in Table I. 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 an oil-heated Brabender Plasticorder (PL 2000-3) mixer with roller-type rotor at a mixer set point temperature of 220°C (i.e., oil bath temperature). The rotor speed was kept at 50 rpm. Nylon-6 was first charged, and, subsequently, the ACM (which were cut into small pieces) was added and mixed for a total time of 10 min. The addition of nylon-6 and ACM into the mixer took approximately 1.5 min in every case. In the case of the compositions containing fillers and plasticizers, ACM was preblended with the fillers and plasticizers in the same Brabender Plasticorder at room temperature with a rotor speed of 70 rpm. During mixing of the blends, both the torque value and the mixer temperature were recorded automatically. After 6 min of mixing, 0.5 phr of HMDC was added to the mixes to cure the rubber phase while blending

Table I Formulation of the Mixes

| Mix No. ^a | A | AB ₁₀ | AB ₂₀ | AB ₃₀ | AC ₃₀ | AS ₃₀ | AP ₁ | AP ₂ |
|--------------------------|-----|------------------|------------------|------------------|------------------|------------------|-----------------|-----------------|
| Nylon-6 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| ACM | 60 | 60 | 60 | 60 | 60 | 60 | 60 | 60 |
| HMDC # 1 ^b | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| N770 | — | 10 | 20 | 30 | — | — | 30 | 30 |
| China clay | — | — | — | — | 30 | — | — | — |
| Ultrasil VN ₃ | — | — | — | — | — | 30 | — | — |
| DOP ^c | — | — | — | — | — | — | 10 | — |
| DBP ^d | — | — | — | — | — | — | — | 10 |

^a All the ingredients except nylon-6 are taken in phr (parts per hundred grams of rubber).

^b Hexamethylene diamine carbamate.

^c Dioctylphthalate.

^d Dibutylphthalate.

(dynamic vulcanization). After completion of the 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 prepare a flat, thin sheet. A similar procedure was followed for all the blends.

Molding

Test specimens (about 1.2 mm thick) were prepared by compression molding at 250°C in a frame-and-plate mold between well-released aluminium foils for 5 min for all the blends and cooled immediately by passing water through the platens under pressure. The samples were removed from the mold when the temperature came down to 110°C. Appropriate test specimens were die cut from the molded sheets and used thereafter.

Rheology

The rheological characteristics of the blends were measured by Monsanto Processability Tester, MPT, with a capillary length to diameter ratio of 30 (30 mm : 1 mm) with an entrance angle of 45 and 60° (compound). The preheat time for each sample was 5 min at the processing temperature. Extrusion studies of the blends were carried out at 250°C. The parameters measured from the experiments were apparent melt viscosity and extrudate die swell; the details of the calculations were given elsewhere.¹⁰

Optical Microscopy

The morphology of the blends was observed by a Metallux 3 Optical Microscope, Leitz, Germany.

The micrographs of the surface of the molded samples were taken at 25°C in reflectance mode under cross-polarization of light. The magnification was varied from 500 to 1000. The average size of the rubber particles was measured with the help of scale attached to the eyepiece.

Mechanical and Dynamic Mechanical Analysis

Tensile tests were performed according to ASTM D 412-89 test method using dumbbell-shaped test pieces, which were punched out from the molded sheets using BS-E-type die. The tests were carried out in a Zwick Universal Testing Machine (UTM) model 1445 at 25 ± 2°C and a crosshead speed of 500 mm/min. The results reported here were the average of three samples. For tension set measurement, the sample was elongated upto 100% at the rate of 50 mm/min at 25°C and kept at that position for 10 min. It was relaxed back to unstressed condition and equilibrated for 24 h. The percentage of change in the length of the sample before and after extension was taken as tension set. For the blends that did not exceed 100% elongation, tension set at break was reported. The hardness of each blend was obtained by ASTM test method D 1706-81 at 25°C.

Dynamic mechanical analysis of the blends 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 to +150°C. The storage modulus E' and loss tangent, $\tan \delta$, were measured for each sample in this temperature range.

Air Ageing Study

Ageing tests were performed in a Multi Cell Ageing Oven of Toyoseiki, Tokyo, Japan, at 175°C for 72 h. After completion of the test, the samples were cooled at room temperature, and the mechanical properties were measured, as described earlier.

Swelling Test

Circular test pieces of radius 20 mm were die cut from the molded sheets. These were weighed accurately and immersed in ASTM oil # 3 at 150°C for 72 h. After completion of swelling, the specimens were removed from the oil, blotted, and weighed quickly in a glass-stoppered bottle. Volume swelling for the specimens was estimated as

$$q - 1 = \left(\frac{W_2}{W_1} - 1 \right) \rho_c / \rho_s \quad (1)$$

where q is the ratio of swollen volume to original unswollen volume ($q - 1 = \% \text{ of volume swell} \div 100$); 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 oil, respectively. The density of the specimens (blends) varied from 1120 to 1140 kg/m³ (calculated on the basis of volume fraction of plastic, rubbers, fillers, and plasticizer). The density of the ASTM oil # 3 at 150°C measured using the standard procedure was 860 kg/m³.

To assess the extent of polymer–filler interaction in the filled rubber mixes swelling tests were carried out in toluene at 35°C. Circular test pieces of 20-mm radius were die cut from the cold-pressed sheets of control ACM and those pre-mixed with 30 phr SRF and 30 phr of silica. The samples were swollen in toluene for 72 h, and the volume swelling of the mixes was estimated by eq. (1), shown above. The density of toluene was taken as 867 kg/m³.

Oil Ageing Test

Tensile test pieces of the blends were immersed in ASTM oil # 3 at 150°C for 72 h. After completion of the ageing, the test specimen were cooled to room temperature and blotted with filter paper. The mechanical properties and hardness of the aged samples were measured at 25°C, as described above.

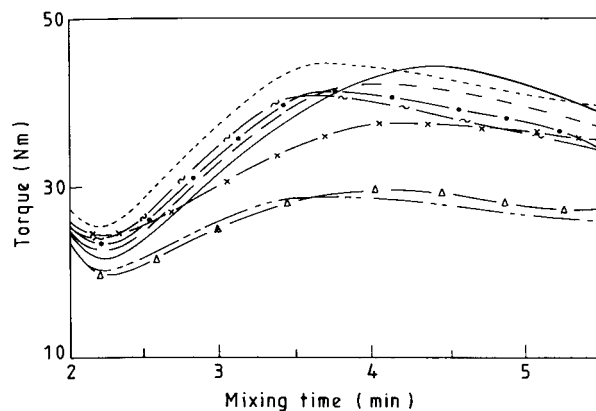


Figure 1 Mixing torque versus time plot of different mixes in Brabender Plasticorder at the mixer set point temperature of 220°C and 50 rpm rotor speed: A (—), AB₁₀ (---), AB₂₀ (—●—), AB₃₀ (—○—), AS₃₀ (—□—), AC₃₀ (—×—), AP₁ (—△—), and AP₂ (—▽—).

RESULTS AND DISCUSSION

Mixing Torque Behavior

The mixing torque behaviors of 40/60 (w/w) nylon-6–ACM blends compounded with various fillers are shown in Figure 1 in the mixing time range of 2–6 min. The very reactive nature of the blend components is evident from the figure, which is manifested in the rise of mixing torque after the initial softening period. It was concluded with the help of infrared (IR) and nuclear magnetic resonance (NMR)⁹ earlier that during melt-blending operation in Brabender Plasticorder at the temperature range of 220–235°C, nylon-6 and ACM chemically interact with each other. The amine and carboxyl acid end groups of nylon-6 react with the reactive epoxy groups (which are present as cure sites) of ACM to form high-molecular-weight graft copolymers, which increase the viscosity of the mixture and, hence, raise the mixing torque. The minimum torque (L_{\min}), the maximum torque (L_{\max}), and the increment of torque ($\Delta L = L_{\max} - L_{\min}$) are also shown in Table II for different mixes. It is clear from the table that with the progressive addition of carbon black, L_{\min} of nylon-6–ACM blend increases. The blend with 30 phr of silica shows the highest L_{\min} value. It is natural that with the progressive addition of fillers, the rubber phase is stiffened; thus, the viscosity of the blend is raised as a whole. However, when the increment of torque (ΔL) values are taken into consideration, it is found that the ΔL value actually decreases with the addition of

Table II Mixing Torque Behavior of the Mixes

| Mix No. | L_{\min} (N m) | L_{\max} (N m) | $\Delta L = L_{\max}$ $- L_{\min}$ (N m) | ΔT^a (°C) |
|------------------|---------------------|---------------------|--|----------------------|
| A | 21.3 | 44.0 | 22.7 | 25 |
| AB ₁₀ | 22.7 | 41.8 | 19.1 | 30 |
| AB ₂₀ | 23.2 | 41.4 | 18.2 | 33 |
| AB ₃₀ | 24.1 | 40.5 | 16.4 | 36 |
| AC ₃₀ | 24.1 | 37.3 | 13.2 | 28 |
| AS ₃₀ | 25.4 | 44.5 | 19.1 | 40 |
| AP ₁ | 19.5 | 29.1 | 9.6 | 27 |
| AP ₂ | 20.0 | 28.6 | 8.6 | 20 |

^a At a mixing time of 9 min.

carbon black loading. The blend filled with 30 phr clay (i.e., Mix AC₃₀) shows the lowest ΔL value, while that with 30 phr of silica (i.e., Mix AS₃₀) shows the highest increment compared to the blend filled with same amount of carbon black. If the increase in torque value suggests the extent of reaction between the polymers, under the above processing conditions, it can be concluded that the addition of fillers reduces the extent of reaction between nylon-6 and ACM in the blends. When 10 phr of different plasticizers, that is, DOP and DBP, are used along with 30 phr of carbon black, the extent of reaction is further reduced with an appreciable lowering of L_{\min} values, as evidenced from Figure 1 and Table II.

The above results suggest that the addition of fillers (carbon black, clay, and silica) into the rubber phase hinders the reactive groups of the above polymer pairs to come in contact; thus, the extent of reaction between them is greatly reduced compared to the blend without any filler. Also, it is probable that the reinforcing filler like carbon black can interact with the rubber through various strong physical forces, thus reducing the effective chemical groups of rubber that would have been otherwise available for reaction with nylon-6. However, the relatively higher ΔL value is noted in the case of silica-filled compounds, which may be attributed to the chemical bond formation between the hydroxyl groups present on silica surface and the epoxy groups of ACM, leading to the higher viscosity of the rubber phase due to increased polymer–filler interaction in the rubber phase. This is also supported by the volume swelling of the uncured ACM mixes filled with 30 phr SRF and 30 phr silica in toluene at 35°C. With the addition of 30 phr SRF, the volume swelling of the

mix is reduced by 13%; whereas with the addition of same amount of silica, about 42% reduction in the volume swelling of the ACM is observed. This clearly indicates greater polymer–filler interaction in the case of silica-filled ACM compared to that of SRF. The possibility of chemical reaction between epoxy groups and hydroxyl groups of silica has been confirmed by Edwards and Sato¹⁴ in the case of silica-filled epoxidized styrene–butadiene rubber (E-SBR).

It is observed that the temperature of the mixer is substantially higher than the mixer set point temperature during the blending process. As shown in the Table II, the amount of fillers and plasticizers has a significant influence on the final temperature of the blend during mixing. The difference in temperature (i.e., ΔT) is the result of higher viscosity of the mixes. The thermal behavior of this system can be described by the model proposed by Scott and Macosko¹⁵ which can be represented as

$$\Gamma \cdot N = h \cdot A \cdot (T_{\text{material}} - T_{\text{wall}}) \quad (2)$$

where Γ is the shaft torque, N is the shaft speed, and A is the surface area of the mixing chamber, which is in contact with the sample. The above equation represents the energy balance on the sample at steady state when the input rate of shaft work (i.e., $\Gamma \cdot N$) is being balanced by heat transfer to the walls of the mixer (here, h represents an overall heat transfer coefficient). Thus, a plot of $\Delta T = (T_{\text{material}} - T_{\text{wall}})$ versus $(\Gamma \cdot N)$ is expected to be a straight line passing through the origin. This plot is given in Figure 2 for all the blends reported in this work at a mixing time of 9 min. All the points are found to lie on a straight line passing through the origin. The above heat transfer model thus adequately describes the thermal behavior of the nylon-6–ACM blends in the batch mixer like a Brabender Plasticorder.

Rheology

Melt Viscosity

The viscosity versus shear stress relationship of different mixes at 250°C is shown in Figure 3. For all the blends, the viscosity decreases with shear stress, suggesting the pseudoplastic nature of the blends. It is evident from the figure that the viscosity of the filled mixes are higher than that of the control unfilled blend at a particular shear stress, though the increment of viscosity with

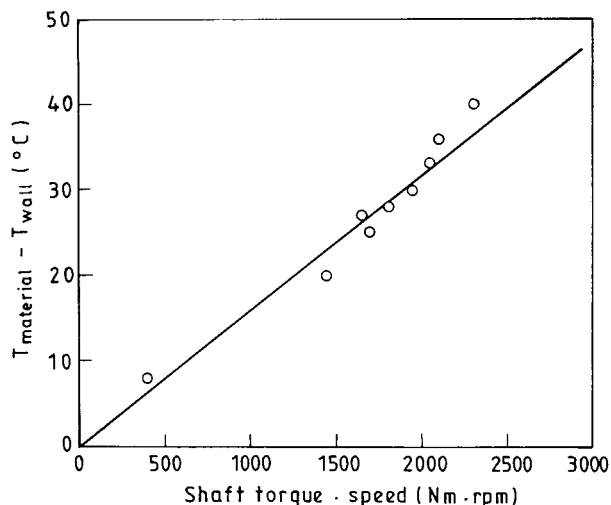


Figure 2 Heat transfer analysis plot of nylon-6-ACM blends; the wall set temperature was 220°C, and the rotor speed was 50 rpm for all the runs.

filler loading is not regular in nature. The silica-filled mix (AS₃₀) shows the highest viscosity. On the other hand, the viscosity of 30-phr black-filled blend decreases with the addition of plasticizers like DOP and DBP. This indicates the plasticization of the mix with both the esters. Similar trend in viscosity is also observed in the equilibrium mixing torque of the above blends in a Brabender Plasticorder after 10 min of mixing time.

It is, however, noted from the appearance of the filled extrudates that an extensive melt fracture occurs during extrusion at high shear rate. This suggests that the addition of fillers reduces the processability of the blends. Similar observations are also made by Coran and Patel.¹² How-

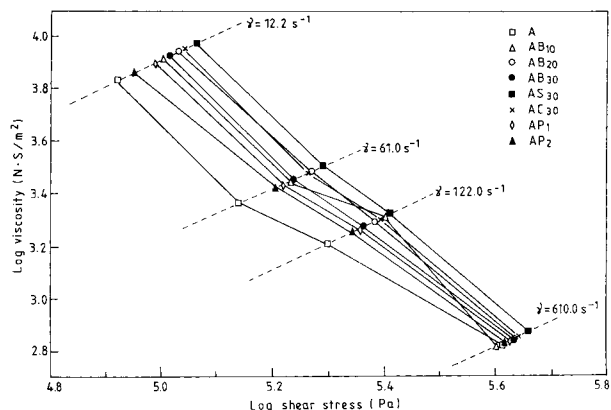


Figure 3 Log viscosity versus log shear stress plot of different mixes at 250°C.

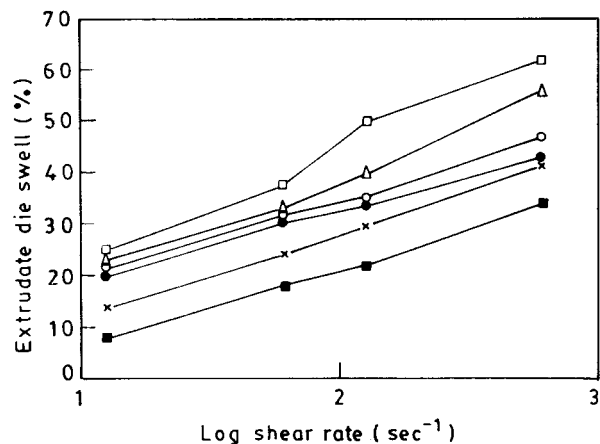


Figure 4 Extrudate die swell versus log shear rate plots of different mixes at 250°C: A (□), AB₁₀ (△), AB₂₀ (○), AB₃₀ (●), AC₃₀ (×), and AS₃₀ (■).

ever, a higher processing temperature (near 260°C) and a lower shear rate alleviate the problem. The processability and fabricability are very much improved with the addition of plasticizers like DOP and DBP in the filled blends.

Extrudate Die Swell

The die swell characteristics of the blends with fillers and plasticizers are shown in Figures 4 and 5, respectively. It is clear from the figures that the

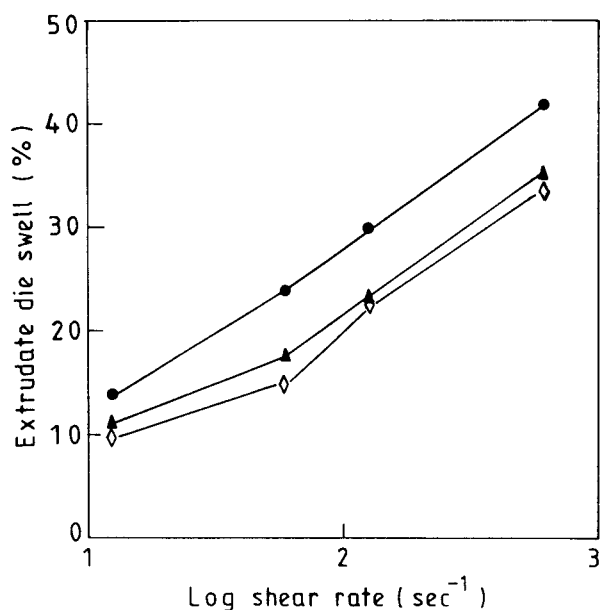


Figure 5 Extrudate die swell versus log shear rate plots of different mixes at 250°C: AB₃₀ (●), AP₁ (▲), and AP₂ (◇).

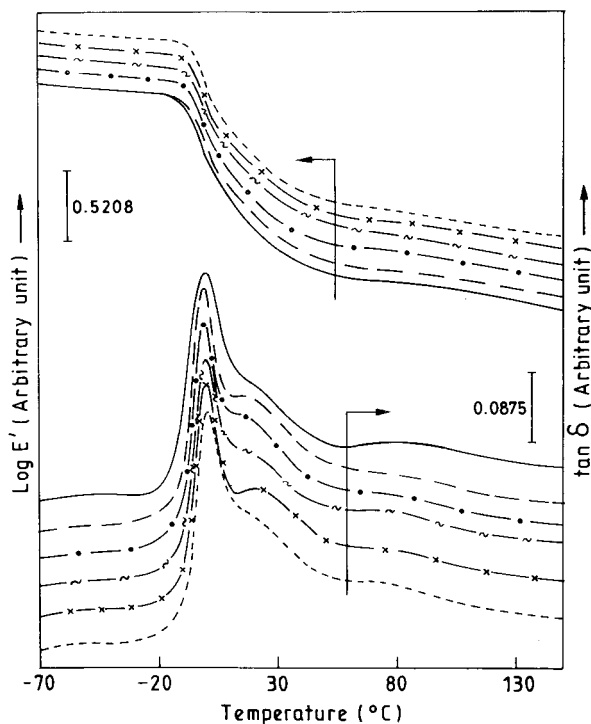


Figure 6 Temperature dependence of dynamic storage modulus (E') and loss tangent ($\tan \delta$) of the blends at 10 Hz frequency: A (—), AB₁₀ (- -), AB₂₀ (-●-), AB₃₀ (-~-), AC₃₀ (-x-), and AS₃₀ (- - -).

die swell increases with increase in shear rate for all the blends. This may be attributed to the considerable increase in the recoverable elastic energy of the system at a higher shear rate.¹⁶ It is interesting to note that with the addition of fillers, the die swell is decreased progressively at a particular shear rate, and the silica-filled mix shows a marked reduction in the die swell values in comparison to the unfilled control blend. As the proportion of rubber in the filled mixes decreases with the increase in filler loading and it is the rubber that contributes to die swell because of its elastic behavior, the filled mixes show reduced die swell values. Polymer–filler interaction would play a great role here: for example, in the case of silica filled blends, the polymer–filler interaction is very high due to the chemical reaction of ACM chains with the surface hydroxyl groups of silica, leading to low die swell of the extrudates. The addition of plasticizers (e.g., DOP and DBP), on the other hand, reduces the die swell characteristics of the filled mix, as shown in Figure 5.

Dynamic Mechanical Thermal Analysis

The dynamic mechanical analysis of the mixes are shown in Figure 6 in terms of temperature

dependence of loss tangent ($\tan \delta$) and storage modulus (E'). The curves are shifted upward for convenience. It is clear from the loss tangent curves that all the blends show the following two main transitions in the temperature range of -70 to 150°C : one sharp peak at 0°C , and another broad peak near 80°C corresponding to the glass transition temperatures of ACM and nylon-6, respectively, confirming the two-phase morphology of the blends. Apart from the above two, a secondary rubber transition is also found at higher temperature side (in the region between 15 – 25°C), which is associated with the restricted relaxation of ACM chains grafted to the nylon-6 matrix.⁹ As discussed earlier, during the melt-blending operation in Brabender Plasticorder in the temperature range of 220 – 235°C , nylon-6 reacts with ACM to form graft copolymers at the interfacial region. The flexibility of the ACM rubber chains when grafted to the plastic matrix is believed 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 boundaries of ACM phase, the formation of which is reflected in the appearance of a new secondary $\tan \delta$ peak in the high-temperature region (between 15 to 30°C). The various parameters measured from the curves are shown in Table III. From the above figures and the table, the following changes are observed.

1. The $\tan \delta_{\max}$ corresponding to the glass transition of the rubber phase of the blends is decreased marginally with the progres-

Table III Dynamic Mechanical Thermal Analysis of the Blends

| Mix No. | $T_{g_r}^a$ ($^\circ\text{C}$) | $\tan \delta_{\max}^b$ | ΔT^c ($^\circ\text{C}$) | $T_{g_p}^d$ ($^\circ\text{C}$) |
|------------------|----------------------------------|------------------------|-----------------------------------|----------------------------------|
| A | -1 | 0.32 | 14 | 87 |
| AB ₁₀ | -1 | 0.33 | 11 | — |
| AB ₂₀ | -1 | 0.31 | 11 | — |
| AB ₃₀ | -1 | 0.30 | 11 | 75 |
| AC ₃₀ | -1 | 0.31 | 11 | 79 |
| AS ₃₀ | 0 | 0.32 | 12 | 74 |
| AP ₁ | -7 | 0.30 | 11 | 85 |
| AP ₂ | -8 | 0.31 | 12 | 85 |

^a Glass transition temperature of the ACM phase.

^b $\tan \delta$ value at the maximum peak position of the rubber phase.

^c Half-width of the $\tan \delta$ peak.

^d Glass transition temperature of the nylon-6 phase.

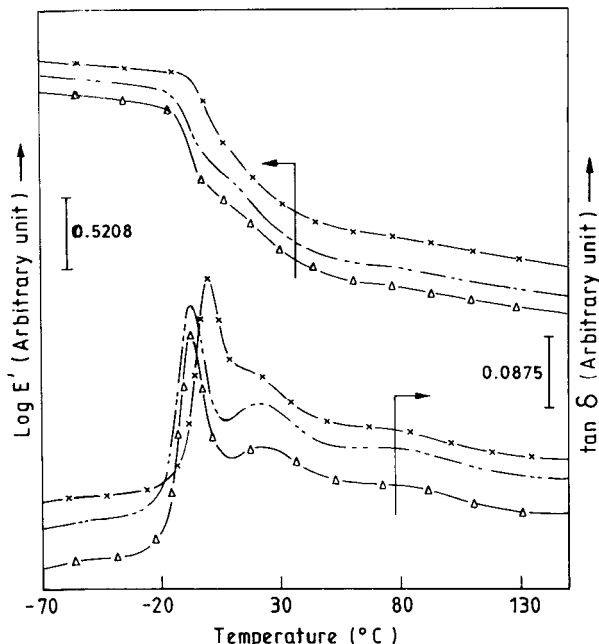


Figure 7 Temperature dependence of dynamic storage modulus (E') and loss tangent ($\tan \delta$) of the mixes at 10 Hz frequency: AB_{30} (-x-), AP_1 (- - -), and AP_2 (-△-).

- sive addition of fillers, although the T_g of ACM is unaffected in all the cases.
2. The filled blends show a lower half-width of the peak compared to that of the unfilled control sample.
 3. The T_g of the nylon-6 phase decreases with the addition of fillers, though the glass transition is not clear in some blends.
 4. The glass transition temperature of the ACM phase in the blends is decreased with plasticizers, while the same of nylon-6 phase is unaffected in the presence of DOP and DBP in the blends.

It is known that the height and width of the loss tangent peak of a filled elastomer is proportional to the weight fraction of filler present in the polymer.¹⁷ Both the height and half-width of the peak decrease with increasing amount of filler. Hence, the above observations (1) and (2) indicate that the fillers preferentially stay in the rubber phase and control its dynamic behavior. On the other hand, result (3) indicates different crystallization characteristics of nylon-6 phase in the presence of filled ACM particles. Nylon-6 being a semicrystalline polymer, the glass transition temperature of its amorphous phase is controlled by

the crystalline index of the polymer.¹⁸ It is probable that in the case of the filled blend of nylon-6 and ACM, the crystallization of nylon-6 phase is hindered due to higher viscosity of the rubber phase¹⁹ compared to that of the unfilled one. Also, a small amount of filler migration into the nylon-6 phase during melt-blending at high shear is possible, which can reduce the crystallinity of it; hence, the T_g of nylon-6 decreases with the addition of fillers. The dynamic storage modulus of the blends, however, does not change much in the above temperature range with the addition of fillers, except for the mix AC_{30} , which registers a higher modulus value compared to that of the unfilled ones. It is argued by Coran that the addition of fillers in the rubber phase increases both the volume fraction of rubber in the blend as well as the stiffness of the rubber phase. These two effects generally cancel each other. Hence, the storage modulus values do not show any appreciable change in the case of the above blends filled with different fillers in the above temperature range. The above trend is also reflected in the modulus behavior of the blends, as discussed later. The decrease in the glass transition of ACM in the blends AP_1 and AP_2 indicate the preferential plasticization of the rubber phase by DOP and DBP. This also results in lower dynamic storage modulus of the blends compared to that of the mix AB_{30} as is found from Figure 7.

Mechanical Properties

The stress-strain curves of various compounds are shown in Figure 8. The tensile strength, elon-

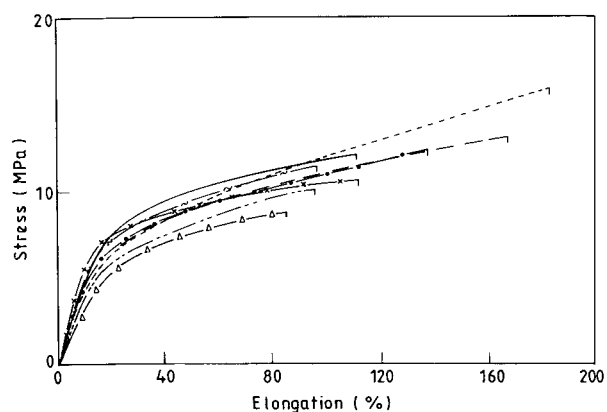


Figure 8 Stress-strain properties of the mixes at room temperature: A (—), AB_{10} (- - -), AB_{20} (—●—), AB_{30} (—○—), AC_{30} (-x-), AS_{30} (- - -), AP_1 (—○—), and AP_2 (-△-).

Table IV Mechanical Properties of Nylon-6-ACM Blends

| Mix No. | Tensile Strength (MPa) | Elongation at Break (%) | Young's Modulus (MPa) | Hardness (Shore-D) | Tension Set (%) |
|------------------|------------------------|-------------------------|-----------------------|--------------------|-------------------|
| A | 12 | 114 | 52 | 44 | 35 |
| AB ₁₀ | 13 | 170 | 44 | 46 | 29 |
| AB ₂₀ | 12 | 140 | 40 | 51 | 24 |
| AB ₃₀ | 11 | 94 | 40 | 54 | (25) ^a |
| AC ₃₀ | 11 | 115 | 52 | 48 | 28 |
| AS ₃₀ | 15 | 183 | 41 | 51 | 23 |
| AP ₁ | 10 | 97 | 33 | 42 | (10) |
| AP ₂ | 8 | 87 | 29 | 39 | (16) |

^a The value in the brackets represents tension set at break.

gation at break, 100% modulus, Young's modulus, hardness, and tension set of the samples are given in Table IV. It is evident that a smaller amount of black addition (10 to 20 phr) improves the elongation properties of the blends without any appreciable change in tensile strength. However, at 30-phr black loading, both the tensile strength and elongation at break decrease compared to that of the unfilled mix. It is interesting to note that the blend with the 30-phr silica (mix AS₃₀) shows the highest extensibility and tensile strength, although the 30-phr clay-filled blend (mix AC₃₀) does not show much change in the mechanical properties. It is also noted that, except for the mix AC₃₀, all the blends show reduced Young's modulus compared to that of the control sample (mix A). However, the hardness of the blends is increased with the addition of fillers. The most outstanding property achieved in the above blends is the improvement of elastic recovery of the blends with the addition of fillers. The tension set of 40/60 control blend reduces from 35 to 23% upon addition of 30-phr silica. The reduction in tension set has been observed for black-filled samples also. The addition of DOP and DBP along with 30-phr black (mixes AP₁ and AP₂, respectively) softens the blend, with an accompanying decrease in tensile strength, modulus, and extensibility. However, the tension set of the blends is decreased with the addition of DOP and DBP, making the blends more elastic or rubbery.

The above observations regarding the effect of fillers in thermoplastic elastomeric rubber-plastic blends are not exactly in line with the results reported by others. Coran⁷ observed that the addition of black or clay to PP-EPDM and nylon-NBR blends reduces in extensibility of the blends with an increase in tension set properties. It is postulated by

Coran that the filler remains in the rubber phase and has the effect of both stiffening the rubber and increasing its volume fraction, as discussed earlier. These two effects are opposite in nature and practically cancel each other. On the contrary, the addition of silica to nylon-6-ACM reactive blends increases about 50% of the extensibility of it with an excellent improvement in the tension set property. It is thought that in the case of above blend of nylon-6 and ACM at the 40/60 (*w/w*) ratio, when fillers are added to the rubber phase, the rubber volume fraction increases progressively leading to greater proximity of the rubber particles or smaller correlation distance. In the case of the blends filled with 30 phr of fillers, the rubber particles practically joined together to form clusters of larger dimensions, which is clear from the optical microscopy of the blend samples, as shown in Figure 9. This change in morphology is practically responsible for imparting elastomeric character in the blends, that is, lower Young's modulus, higher extensibility and lower tension set. The average domain sizes of the rubber phase in the mixes are in the range of 2–10 μm .

Addition of plasticizer, along with 30 phr of black, ultimately reduces the strength of the rubber phase; hence, the mechanical integrity of the blends is worsened as a whole. In the case of silica-filled mix, the excellent improvement in rubber characteristics of the blend can be envisaged in light of the chemical reaction of ACM chains with the surface hydroxyl groups of silica at a high temperature of mixing, leading to higher polymer-filler interaction, as suggested earlier.

The difference in the behavior of filled PP-EPDM and nylon-6-NBR with that of nylon-6-ACM thermoplastic elastomeric blends can be ex-

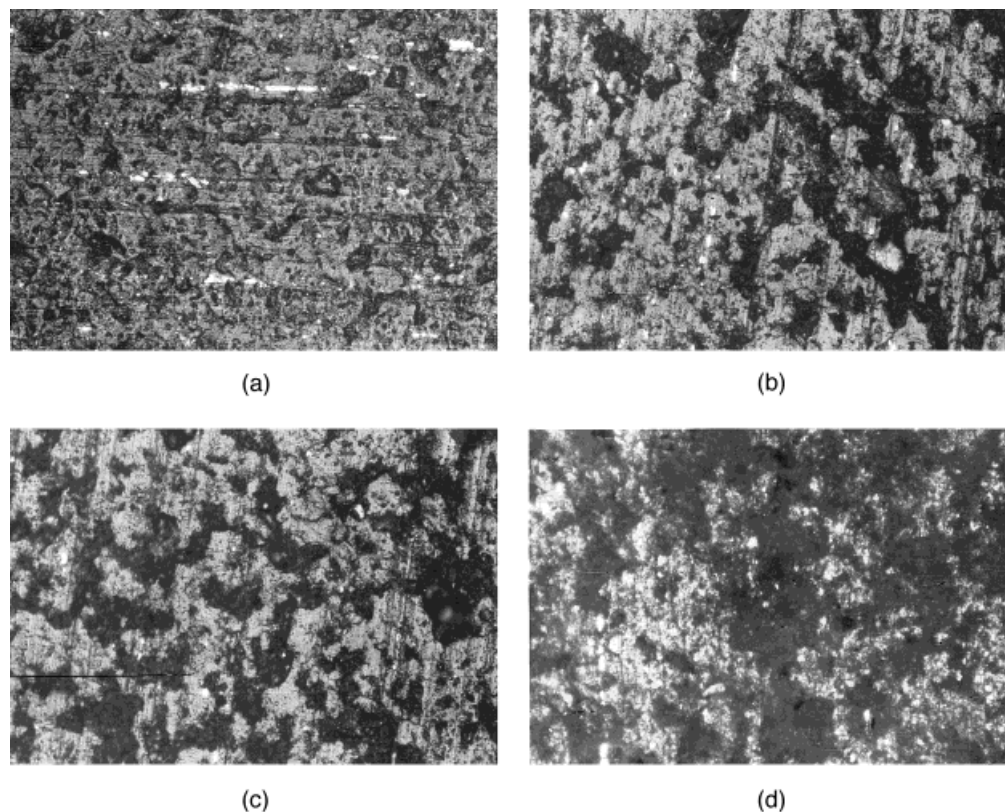


Figure 9 Optical microscopy of the blends ($\times 500$ magnification): (a) A, (b) AB_{10} , (c) AB_{20} , and (d) AB_{30} .

plained on the basis of the reactive nature of the later blend system. It is probable that in the case of PP-EPDM and nylon-6-NBR, which are non-interactive in nature, the fillers may migrate into the region of interfacial area of contact between the rubber and plastic phase during the melt-blending process, thus reducing the compatibility between the two component phases. Thus, the mechanical properties are reduced compared to the unfilled blends. On the other hand, nylon-6-ACM graft copolymer formed during melt-blending, even in the filled mixes (as discussed in mixing torque behavior of the blends), is enough for technological compatibilization of the blend components. Hence, in the above case, no drastic reduction of the mechanical integrity of the blends is observed with the addition of fillers.

Heat and Oil Resistance

Table V shows the mechanical properties of the blends before and after ageing in air at 175°C for 72 h and in ASTM oil # 3 at 150°C for 72 h. The volume swell percentage in ASTM oil # 3 at the same condition is also shown in the same table.

It is surprising to note that the addition of low amount of C-black increases the volume swelling of the blend. However, with increasing amount of black in the blend, the swelling percentage is decreased again. For the silica-filled system, the volume swelling shows the least value. It is described²⁰ that the extent of swelling of a blend in a particular solvent depends upon the structure of the polymer phases and can be related to the properties of the polymer chains, such as molecular mobility, phase interaction, and so on. As the fillers preferentially reinforces the rubber phase, its introduction should reduce the volume swell of the ACM phase and, thus, reduces the overall volume swell of the blends in oil. However, an opposite result is obtained; that is, volume swell is increased with the addition of black and clay in the blend, which can be explained on the basis of the following: (1) development of lower crystallinity of nylon-6 phase in the filled blends, as discussed earlier, which can give rise to high volume swell of the blends; (2) increased rubber volume fraction in the filled blends (the rubber phase showing lower swelling resistance than nylon-6).

Table V Heat and Oil Resistance of Nylon-6-ACM Blends

| Mix No. | A | AB ₁₀ | AB ₂₀ | AB ₃₀ | AC ₃₀ | AS ₃₀ | AP ₁ | AP ₂ |
|-------------------------------------|-----|------------------|------------------|------------------|------------------|------------------|-----------------|-----------------|
| Unaged samples | | | | | | | | |
| TS (MPa) | 12 | 13 | 12 | 11 | 11 | 15 | 10 | 8 |
| Elongation at break (%) | 114 | 170 | 140 | 94 | 115 | 183 | 97 | 87 |
| Hardness (Shore A) | 44 | 46 | 51 | 54 | 48 | 51 | 42 | 39 |
| Oil ageing at 150°C in ASTM oil # 3 | | | | | | | | |
| Volume swell (%) | 3 | 8 | 6 | 5 | 7 | 2 | 4 | 2 |
| TS (MPa) | 12 | 14 | 14 | 13 | 11 | 16 | 11 | 10 |
| Elongation at break (%) | 70 | 94 | 74 | 62 | 60 | 113 | 75 | 55 |
| Hardness (Shore A) | 46 | 47 | 49 | 50 | 47 | 56 | 44 | 44 |
| Ageing at 175°C for 72 h | | | | | | | | |
| TS (MPa) | 10 | 12 | 13 | 12 | 13 | 18 | 11 | 8 |
| Elongation at break (%) | 100 | 31 | 40 | 30 | 46 | 60 | 40 | 15 |
| Hardness (Shore A) | 46 | 46 | 49 | 50 | 47 | 52 | 47 | 48 |

In the case of silica-filled system, the ACM chains are grafted to silica surface through chemical reaction during melt-blending, which leads to high polymer–filler interaction. This results in very low volume swelling of the blend in ASTM oil # 3 at a higher temperature. Also, for the black- and clay-filled blends, the volume swelling is well below 10%, which suggests the excellent hot oil resistance of the filled blends. Coran and Patel²¹ reported a volume swell of 22% at 100°C in ASTM oil # 3 for NBR–PP (50 : 50 by weight) thermoplastic vulcanizates, which is higher than that of the above filled blends.

The mechanical properties of the blends after air ageing at 175°C for 72 h as well as after oil ageing at 150°C for 72 h are shown in Table V. It is clear that the hardness and the tensile strength of the blends remain practically unchanged after ageing in both the conditions. However, a marked reduction in the elongation at break is observed after ageing for the filled blends. The abrupt reduction of the extensibility is probably due to the reduced crystallinity of the nylon-6 (main matrix) phase, which increases the diffusion of active oxygen into the matrix during ageing and accelerate the degradation process. We think that proper selection and the use of antioxidant package can alleviate this problem and can improve the ageing resistance of the filled thermoplastic elastomers based on the nylon-6 and ACM blends.

CONCLUSIONS

Melt blending of nylon-6 and acrylate rubber (ACM) in an internal mixer like a Brabender

Plasticorder in the temperature range of 220–235°C presents a unique way for the preparation of a novel heat and oil resistant thermoplastic elastomers. The blends show excellent resistance to oil swelling at elevated temperature (e.g., 150°C), and its service temperature range can be extended up to 170–200°C without much deterioration of the mechanical properties. In this article, an investigation was carried out to find out the effect of various fillers and plasticizers on the key performances of such blends. The following conclusions can be drawn from the above studies.

1. The addition of carbon black and clay reduces the extent of reaction between nylon-6 and acrylate rubber, while silica interacts with ACM chains through covalent bond formation, which increases the overall polymer–filler interaction in the blends.
2. The viscosity of the filled blends is higher than that of the control unfilled blend. However, addition of ester plasticizer lowers the viscosity and improves the processability.
3. The addition of fillers does not change the glass transition temperature of the ACM phase, but the T_g of the nylon-6 phase is reduced in the filled blends, probably due to a decrease in its percentage of crystallinity. However, a substantial improvement in the damping properties of the blends in the service temperature range (25 to 175°C) is revealed from the dynamic mechanical thermal analysis results.
4. Mechanical properties of the blends are improved very much with the addition of lower amount of carbon black (i.e., 10 to 20 phr)

and the higher percentage of silica (30 phr). The extensibility of the blends is increased by 50% with the addition of silica due to higher polymer–filler interaction. Also, the elastic recovery of the blend is very much improved in the case of filled samples. The improvement in the overall mechanical integrity of the blends is probably due to the formation of co-continuous morphology of rubber and plastic, which is evident from the optical micrographs of the blends.

5. The oil swelling resistance of the above blends is actually decreased slightly with the addition of fillers, except that for the silica-filled system. However, the volume swell in ASTM oil # 3 at 150°C of the blends is well below 10%, which suggests its excellent hot-oil resistance.

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