

## ***Influence of Level of Interaction on the Mechanical and Dynamic Mechanical Properties of Thermoplastic Elastomers<sup>†</sup>***

ANIL K. BHOWMICK<sup>\*#</sup> AND ABHIJIT JHA<sup>\*</sup>

*Nylon-6 and acrylate rubber (ACM) were melt-blended in a Brabender Plasticorder at 220°C and 40 r.p.m. rotor speed. The reactive nature of the blend is reflected in the mixing torque behaviour of the blends at different compositions. The solubility characteristics of the blends in formic acid solution gives an approximate idea of the amount of nylon-6 grafted onto ACM and vice-versa. The influence of interaction between the two polymers on the mechanical and the dynamic mechanical properties of the blends are analysed in details and the results are interpreted on the basis of the formation of nylon-ACM graft copolymer at the interfaces. The dynamic mechanical thermal analysis (DMTA) reveals a two-phase morphological structure, indicating incompatibility of the blend components. The grafting reaction results in dramatic increase in both the storage modulus and the Young's modulus of blends. The presence of grafted rubber chains is reflected in the secondary transition of the rubber loss peak at higher temperature. Also, a substantial improvement in the damping properties of the blends in the service temperature range (i.e., 25°C to 175°C) is revealed from the DMTA results. The dynamic vulcanisation of the ACM phase during melt-mixing improves the elongation at break values of the blends.*

Reactive blending is known to be one of the most important processes of compatibilisation of two or more immiscible polymers<sup>1–3</sup>. The two polymers, functionalised with proper reactive groups on their chains react to each other at the interface during mixing at selective temperatures to generate a copolymer which compatibilises the two phases. Coran<sup>4</sup> reported the properties of thermoplastic elastomers from polyamides/chlorinated polyethylene (CPE) reactive blends. In this paper, we report our observations on the reactive blends of nylon-6 and acrylate rubber (ACM), where the amine

or carboxyl end groups of nylon-6 are expected to react with the reactive epoxy groups of ACM to produce the necessary graft copolymer at the interface during melt-blending operation. The influence of the interfacial reaction on the mechanical and dynamic mechanical properties is highlighted.

### EXPERIMENTS

Nylon-6 (*Ultramid B3*) of BASF, GERMANY and acrylate rubber (*NIPOL AR51*) of Nippon Zeon Co. Ltd., Japan and *DIAK#1* of Du Pont

<sup>†</sup> Paper presented at the International Rubber Conference 1997 Malaysia, 6–9 October, Kuala Lumpur

<sup>\*</sup> Rubber Technology Centre, Indian Institute of Technology, Kharagpur, P.O. Box 721 302, India

<sup>#</sup> Corresponding author

were used for the work. The blends were prepared in batches of 50 gm polymer in a Brabender Plasticorder (PL2000-3) mixer with roller type rotor at a mixer set point temperature of 220°C. The rotor speed was kept at 40 r.p.m. The change of mixing torque with mixing time along with the stock temperature was recorded for each blend. During dynamic vulcanisation, 0.5 phr. DIAK#1 was added to the blends after 8 min of mixing and the mixing was continued for another 5 min after DIAK#1 addition. Test specimens (about 1.2 mm thick) were prepared by compression moulding at 230°C in a frame-and-plate mould between well released aluminium foils for 2 min for all the samples and immediately cooled by passing water under pressure. Solubility of the blend samples was measured in 85% formic acid solution at room temperature and the weight percent of unextracted nylon-6 was calculated. Tensile tests were performed according to ASTM D412-80 in a Zwick Universal Testing machine (UTM), model 1445. Dynamic mechanical thermal analysis was carried out in a DMTA Rheometric Scientific MK-II model in the blending dual cantilever mode at a frequency of 10 Hz and at a heating rate of 2°C/min.

## RESULTS AND DISCUSSION

The reactive nature of nylon-6 and ACM blend is manifested in the mixing torque behaviour of the blends in Brabender Plasticorder at 220°C. Both pure nylon-6 and ACM show a gradual decline in torque (*Figure 1*) with a rise in stock temperature until both reach a steady-state value. But in the case of nylon-6/ACM blends, the mixing torque shows an upward trend after the initial softening (*Figure 1*). This increase in torque can be attributed to the interfacial reaction which may occur between

the two polymers at the processing conditions<sup>5,6</sup>. During mixing, the melt reaction between the two polymers results in an increase in molecular weight and, therefore, the viscosity of the mix, which raises the torque during mixing. It is also interesting to note that the increment in torque values (*i.e.*, maximum torque minus the minimum torque) when plotted against the weight fraction of ACM (*Figure 2*), passes through a maximum point corresponding to a composition of 55/45 nylon-6/ACM weight ratio. If the increase in torque value suggests the extent of reaction of the polymers, it can be assumed that maximum amount of reaction occurs in the blends with 45 weight percent of ACM. Proportion of ACM on either side of the 45% results in less grafted polymers and hence, lower increment in torque. The solubility data also supports the above observation. The amount of unextracted nylon-6 in formic acid (which is approximately equal to the weight percentage of nylon-6 grafted to ACM chains) of the nylon-6/ACM blends, both dynamically vulcanised and without dynamic vulcanisation, suggests that maximum amount of graft formation occurs near 50/50 (w/w) blend ratio (*Figure 3*).

*Figure 4* represents the DMTA results of pure ACM, nylon-6 and 50:50 (w/w) blend of nylon-6/ACM in terms of temperature dependence of  $\tan \delta$  in the range between -100°C to 150°C. The blend shows two main damping peaks, one at -2.5°C corresponding to the  $T_g$  of ACM ( $T_g$  of pure ACM = 0°C) and another broad peak at 85°C due to  $T_g$  of nylon-6 ( $T_g$  of pure nylon-6 = 98°C). Though peak positions are shifted compared to that of the homopolymers due to interaction between the components, the appearance of two separate  $\tan \delta$  peaks suggests the microheterogeneity of the blend (*i.e.*, two-phase morphological structure).

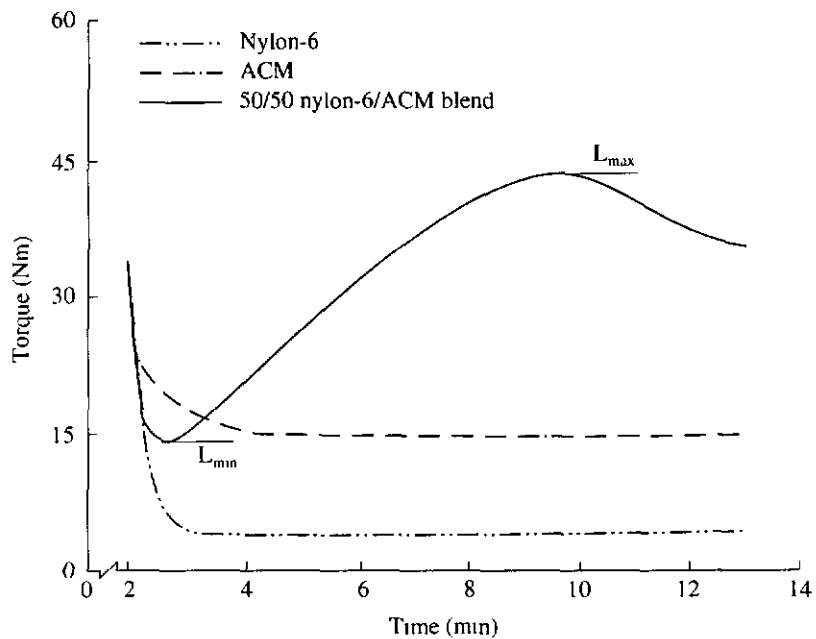


Figure 1. Mixing torque vs. time plot at 220°C and 40 r.p.m. rotor speed.

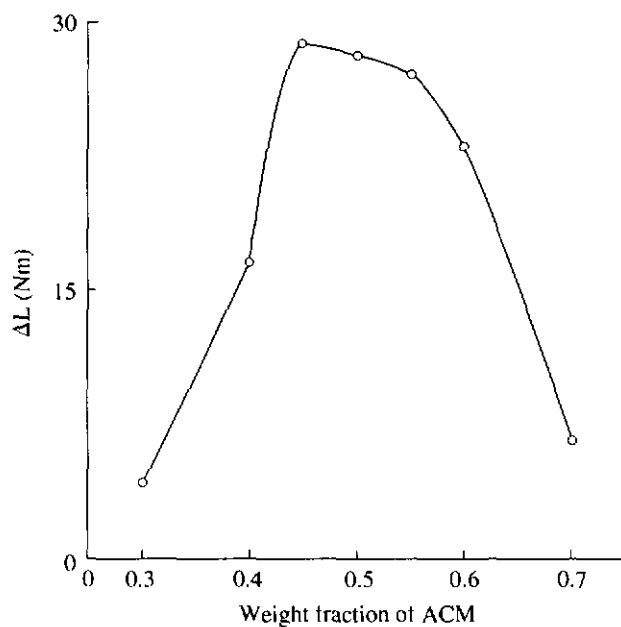


Figure 2 Increment in mixing torque vs. weight fraction of ACM in the blend

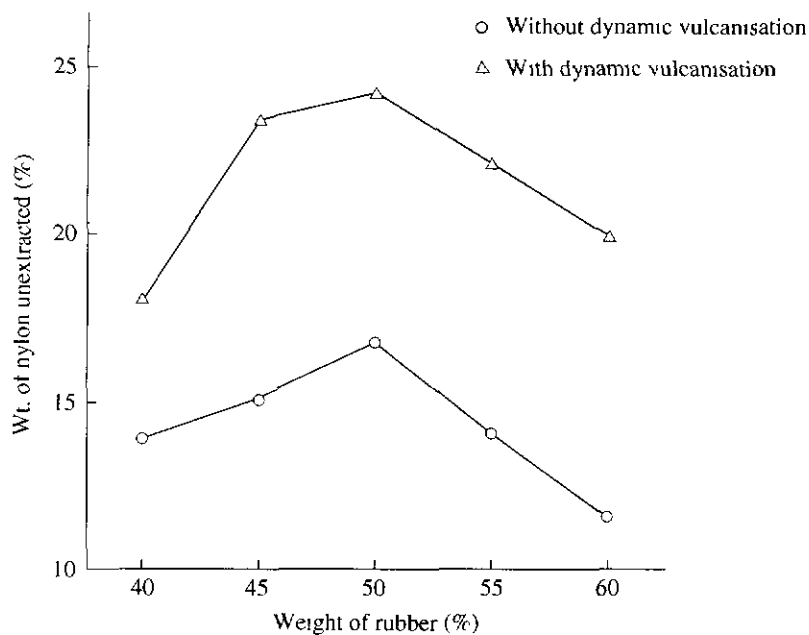


Figure 3. Weight percentage of nylon grafted vs weight fraction of ACM in the blends.

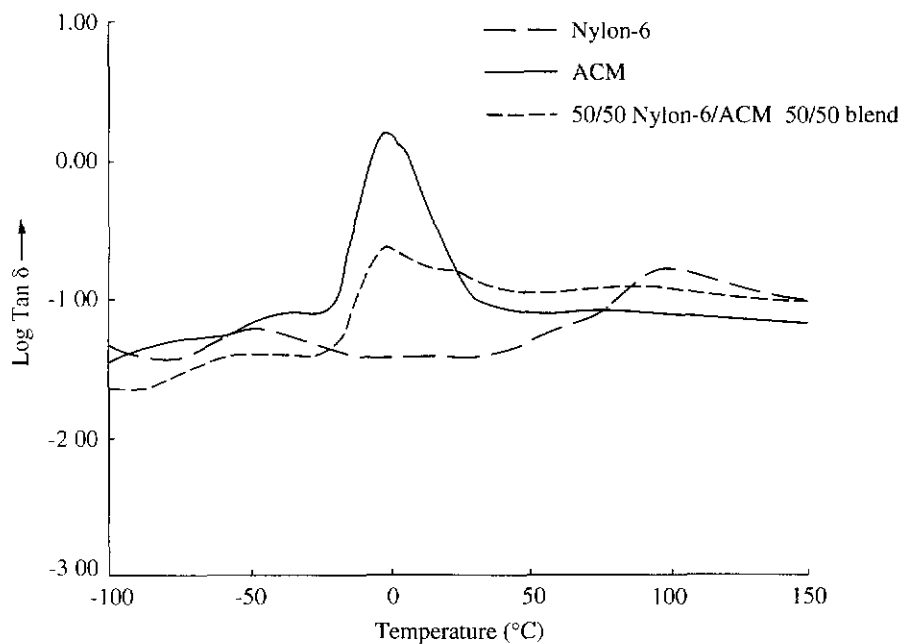


Figure 4. Temperature dependence of loss tangent

To study the effect of interaction on the dynamic mechanical properties of the blends, the mixing has been carried out to different extents (*i.e.*, for different durations) for 40:60 (w/w) blend and the moulded samples are analysed under identical conditions. *Figure 5* summarises the temperature dependence of  $\tan \delta$  and storage moduli, respectively. The  $\tan \delta_{\max}$  ( $\tan \delta$  at peak position) and the  $T_g$  of the ACM phase decrease progressively upto 9 min – 11 min and then increase marginally.  $T_g$  of nylon-6 phase displays a progressive decreasing trend with mixing time. The most interesting feature observed in the above case is the appearance of a secondary  $\tan \delta$  peak of the rubber phase at high temperature region with increasing level of interaction. In the blends with 9 min 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. This is also reflected in the modulus vs. temperature plot (*Figure 5*). As the height of the dynamic transition of a component of a composite apparently reflects the relative quantity of the component itself<sup>7</sup>, the decrease of  $\tan \delta_{\max}$  of ACM in the blend is the result of a reduction of the relative quantity of bulk rubber 'active' in the dynamic transition. Since the weight fraction of ACM in these blends is constant, the above result can be interpreted by assuming that as the level of grafting increases with mixing time, the relative quantity of bulk rubber is reduced resulting in the reduction of the  $\tan \delta_{\max}$  values. The decrease in  $T_g$  of ACM phase with interaction can be explained in the light of thermal stress built-up in the outer shell of each of the rubber particles during moulding/cooling due to greater thermal contraction of rubber compared to the glassy matrix. This thermal stress can only be developed when there is

sufficient adhesion between the two phases, generally believed to be secured by the usual grafting operation. As a consequence of this, the free volume of rubber increases and results in a decrease in the glass transition temperature<sup>8</sup>. The decrease in  $T_g$  of nylon-6 can also be explained on the basis of the above arguments. It is reported that the segmental motion in chains of a polymer when attached to a more mobile component (*i.e.*, lower  $T_g$ ) is enhanced in the blend compared to that in the homopolymer. As nylon-6 is grafted to ACM chains which are rubbery in nature, the flexibility of the nylon chains is increased leading to a decrease in its  $T_g$  values.

*Figure 6* shows the DMTA results of nylon-6/ACM blends with varying amount of rubber content in terms of  $\tan \delta$  vs. temperature (both dynamically vulcanised and without dynamic vulcanisation). It is clear from the figure, that in case of unvulcanised blends, the  $\tan \delta_{\max}$  of the ACM phase increases progressively with increasing amount of rubber content (which is evident from the earlier discussion) and  $T_g$  of ACM decreases with increasing plastic content in the blends. As the nylon-6 content in the blends is increased, the radii of the rubber particles are reduced leading to larger interfacial contact area per unit volume of rubber. This results in greater adhesion between the two phases and hence more inclusion of free volume in the rubber phase due to differential thermal stresses developed during cooling. As a result, the  $T_g$  of ACM phase decreases with increasing plastic content in the reactive blends. In case of dynamically vulcanised blends, two changes are observed due to crosslinking of the rubber phase: (i) the reduction in the flexibility of the bulk rubber chains leading to higher  $T_g$  values compared

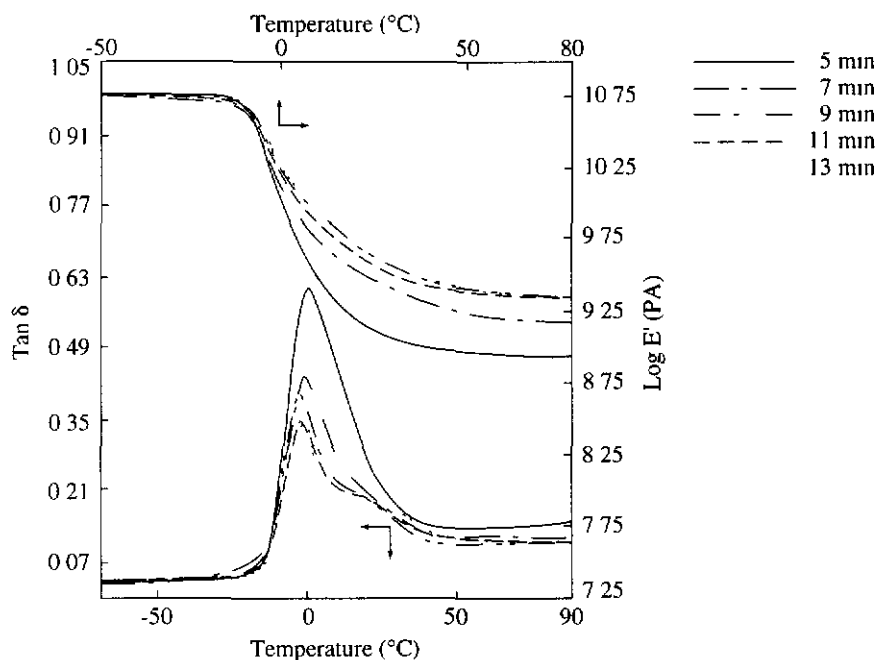


Figure 5 Temperature dependence of  $\tan \delta$  and  $E'$  of Nylon-6/ACM (40/60) blends interacted for different times

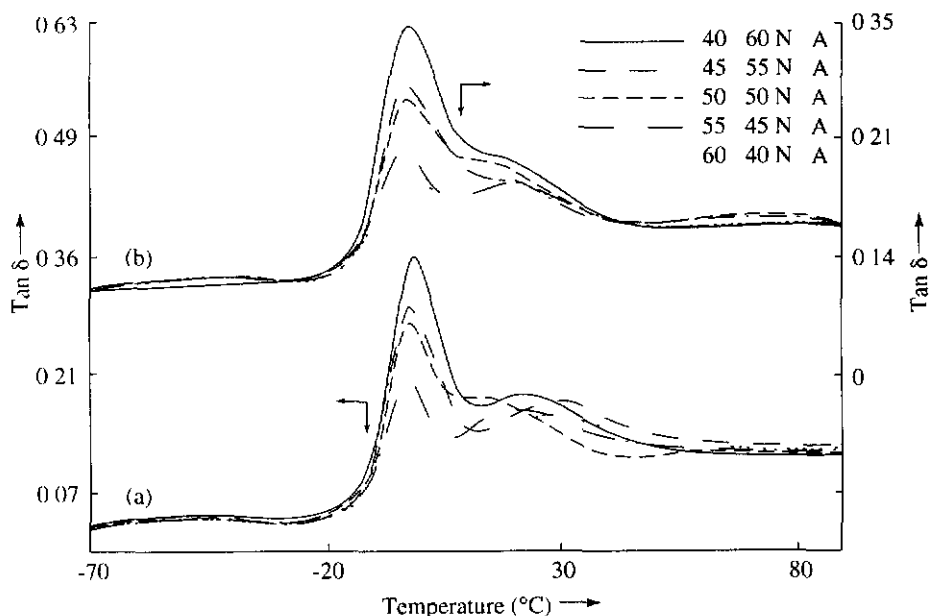


Figure 6 Temperature dependence of  $\tan \delta$  of Nylon-6/ACM blends with different plastic to rubber weight ratio without dynamic vulcanisation (a) and the blends with dynamic vulcanisation (b)

to that of the blends without dynamic vulcanisation, and (ii) the broadening of the loss tangent peak of the rubber phase with a reduction in the height. The effect is more prominent in the blends with higher amount of plastic content.

The mechanical properties of the 40/60 nylon-6/ACM blends are given in *Table 1*. It is observed that both the tensile strength and elongation at break increases as the time of reaction increases. Also, the Young's modulus and the hardness increases progressively to higher values. As the rubber content of this blend is fixed, the increasing trend in mechanical properties is very likely due to interfacial reaction between the two phases, which enhances the adhesion between the two components. It is important to note that both the Young's modulus and the tensile strength of the blend with 13 min of reaction time show an appreciably higher values, resembling that of highly reinforced elastomer systems.

In the case of thermoplastic elastomeric blends with higher amount of plastic content, the tensile strength reaches a value of 19 MPa – 20 MPa and an elongation of about 100% –

120% (*Table 2*). These blends, when dynamically vulcanised, display an increased elongation at break and enhanced tensile strength. However, the Young's moduli and the hardness of the blends are decreased slightly due to vulcanisation.

## CONCLUSIONS

Nylon-6 and ACM react to each other in Brabender Plasticorder at 220°C which is manifested in the rise of mixing torque during melt-blending operation. This is also supported by the fact that certain proportions of the nylon-6 in the blends remain insoluble in the formic acid solutions. In the dynamic mechanical analysis, it is observed that both the  $\tan \delta_{\max}$  and the  $T_g$  of the bulk rubber phase decreased with level of interaction between the two phases which are followed by the appearance of a secondary rubber transition at the higher temperature region (13°C to 22.5°C) for 40/60 nylon-6/ACM (w/w) blend. The interaction increases the Young's modulus and the hardness to an appreciable extent. Also, the tensile strength and the elongation at break increases with the level of reaction. Dynamic

TABLE 1. MECHANICAL PROPERTIES OF 40/60 (W/W) NYLON-6/ACM BLEND

Reaction time <sup>a</sup> (min)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Hardness (Shore-D)
5	4	50	20.0	35
7	7	84	23.0	42
9	6	60	29.0	44
11	5	40	29.0	47
13	12	96	37.0	48

<sup>a</sup>Mixing time at 220°C/40 r.p.m. + 2 min moulding time at 230°C, 10 MPa pressure

TABLE 2 MECHANICAL PROPERTIES OF NYLON-6/ACM BLENDS WITH AND WITHOUT DYNAMIC VULCANISATION<sup>a</sup>

Weight percentage of plastic (%)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Hardness (Shore-D)
40	12(10) <sup>b</sup>	96(122)	37(30)	48(44)
45	13(13)	90(142)	41(35)	50(47)
50	12(15)	92(140)	45(43)	55(51)
55	19(16)	120(116)	62(56)	57(54)
60	17(20)	100(150)	71(68)	60(57)

<sup>a</sup>Vulcanised with 0.5 p.h r. of HMDC<sup>b</sup>The values in the parenthesis indicate the properties corresponding to the dynamically vulcanised blends.

vulcanisation of the blends results in a slight reduction in hardness, Young's modulus, but the tensile strength and the elongation at break increase.

## ACKNOWLEDGEMENT

The authors are grateful to the Department of Science and Technology, New Delhi, India for funding the project.

## REFERENCES

1. XANTHOS, M (Ed.)(1992) *Reactive Extrusion, Principles and Practice*. Munich: Hanser
2. CORAN, A Y. (1988) *Handbook of Elastomers – New Developments and Technology* (Bhowmick A K and Stephens H.L eds.). New York: Marcel Dekker Inc
3. LEGGE, N R., HOLDEN, G AND SCHROEDER, H E (Eds.)(1987) *Thermoplastic Elastomers – A Comprehensive Review*. Munich: Hanser
4. CORAN, A Y AND PATEL, R (1983) *Rubb Chem Technol.*, **56**, 210.
5. BAKER, W E AND SALEEM, M (1987) *Polymer*, **28**, 2057.
6. OSHINSKI, A, KESKKULA, H AND PAUL, D R (1992) *Polymer*, **33**, 268
7. DICKIE, R A. (1978) *Polymer Blends* (Paul D R and Newman S eds) Volume I New York: Academic Press.
8. RICCO, T, PAVAN, A AND DANUSSO, F (1959) *Polymer*, **16**, 685.