Mechanical and Dynamic Mechanical Thermal Properties of Heat- and Oil-Resistant Thermoplastic Elastomeric Blends of Poly(butylene terephthalate) and Acrylate Rubber

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ABSTRACT: Poly(butylene terephthalate) (PBT) and acrylate rubber (ACM) were melt-blended in a Brabender Plasticorder at 220°C and 40 rpm rotor speed. The blends were dynamically vulcanized by the addition of hexamethylenediamine carbamate (HMDC) during the melt-blending operation in the Brabender. Dynamic mechanical thermal analysis (DMTA) of the blends suggests a two-phase morphology of the blends with two separate T_g's for both components. The blends were also compatibilized by the addition of a dibutyl tin dilaurate (DBTDL) catalyst, which enhanced the extent of the transesterification reaction between the two polymers. The transreaction results in softer blends with higher elongation properties. The above blends also show very good oil and heat resistance at elevated temperatures. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1001–1008, 2000

Key words: poly(butylene terephthalate); acrylate rubber; thermoplastic elastomer; rubber–plastic blends; heat resistance; oil resistance

INTRODUCTION

Thermoplastic elastomers (TPEs) prepared from rubber–plastic blends have gained considerable interest in recent years.[1–3] They offer the simplest route to achieve outstanding properties at low cost. A wide range of properties can be tailormade 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, a wide variety of performances can be provided to meet diverse industrial applications in a cost-effective way. Several researchers reported on thermoplastic elastomeric rubber–plastic blends. If one follows the development and emergence of the new class of TPEs in the last few decades, it is clear that preparation of suitable thermoplastic elastomeric blends of rubber and plastics with improved heat- and oil-resistant properties is the present trend of progress.

Most of the TPEs prepared so far from rubber–plastic blends have poor high-temperature properties. For example, commercial blends based on EPDM–PP, NBR–PP, and Alcryn melt-processible rubber have a maximum operating temperature of 125°C. Coran[4] reported that TPEs could be made using plastic of a high melting point and, thereby, the operating temperature may be enhanced. However, at the high melting and processing temperature of plastics, many rubbers tend to degrade. Also, many high-melting plastics like polyamides present some interesting process-

ing problems, somewhat like those involved in perfluorocarbon resins. Many high-temperature rubbers like silicones, which can withstand high temperature, do not have an appropriate match of hard segments in a blend. The problems are still aggravated when chemical and oil resistance are demanded from such TPEs. It is with this background that the present investigation was initiated.

The objective of the present work was to develop novel heat- and oil-resistant thermoplastic elastomeric blends of rubber and plastic with improved performances. Poly(butylene terephthalate) (PBT) was chosen as the plastic component of the blends, as it has a high melting temperature, for example, 225°C, and thus can be used at a higher service temperature range without any appreciable loss in the mechanical properties of the blends. Also, PBT, being highly crystalline in nature, can provide very good solvent and oil resistance to the blends. Polyacrylate rubber (ACM), which is known to be an excellent heat- and oil-resistant rubber, may be used to impart both heat and oil resistance at an elevated service temperature. Venkataswamy and Payne[5,6] reported oil-resistant thermoplastic elastomeric alloys for high-temperature use. Recently, we reported the development and properties of novel heat- and oil-resistant TPEs from the reactive blends of nylon-6 and ACM.[7–9] In this article, the mechanical and dynamic mechanical thermal properties of heat- and oil-resistant thermoplastic elastomeric blends of PBT and ACM are discussed.

EXPERIMENTAL

Materials

PBT (Ultradur A3) in pellet form (melting point: 223°C) was supplied by BASF (Germany). ACM, NIPOL AR51 (sp gr = 1.1 at 25°C) was obtained from the Nippon Zeon Co. Ltd. (Tokyo, Japan). It was reported to have an epoxy cure site and was made from the ethyl acrylate monomer. Hexamethylenediamine carbamate (HMDC) DIAK#1 (DuPont), used as a crosslinking agent for ACM, was supplied by NICCO Corp. (India). Dibutyl tin dilaurate (DBTDL), which is known to be a catalyst for a transesterification reaction between two esters, was supplied by the NICCO Corp.

Preparation of the Blends

The formulations of the different mixes are given in Table I. PBT and ACM were dried at 100°C for

Table I   Formulation of the Mixes

| Ingredient | Mix No. | | | | |
	A$_1$	A$_2$	A$_3$	A$_2$C	A$_2$D
PBT	40	35	30	35	35
ACM	60	65	70	65	65
HMDC[a]	0.5	0.5	0.5	0.5	1.0
DBTDL[b]	—	—	—	0.1	—

[a] HMDC is in phr (parts per hundred grams of rubber).
[b] Taken as weight percent of the total mix.

24 h in a vacuum 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 40 rpm. PBT was first charged and, subsequently, ACM (which was cut into small pieces) was added and mixed for a total time of 10 min. The addition of PBT and ACM into the mixer took approximately 1.5 min in every case. After 6 min of mixing, 0.5 phr of HMDC was added to the mixes to cure the rubber phase while blending (dynamic vulcanization). In the case of the compositions containing DBTDL, ACM was preblended with the catalyst in the same Brabender Plasticorder at room temperature with a rotor speed of 70 rpm. 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 aluminum 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 was decreased to 100°C. Appropriate test specimens were die cut from the molded sheets and used thereafter.

Mechanical and Dynamic Mechanical Analysis

Tensile tests were performed according to the ASTM D 412-93 test method using dumbbell-shaped test pieces which were punched out from
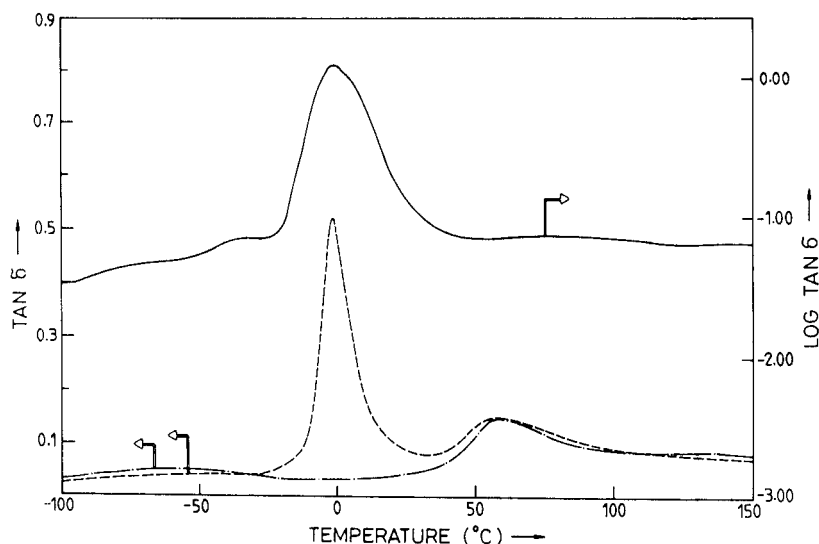
Figure 1 Temperature dependence of loss tangent (tan δ) of the blends at 10-Hz frequency: (—) ACM; (– · –) PBT; (- - - -) A_1.

the molded sheets using a 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 are the average of three samples. The hardness of each blend was obtained by the ASTM test method D 1706-81 at 25°C.

Dynamic mechanical analysis of the blends as well as that of the pure homopolymers was performed on a DMTA Rheometric Scientific MK-II model in a 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 storage modulus, E', loss modulus, E'', and loss tangent, tan δ, were measured for each sample in this temperature range. The data were analyzed using a COMPAQ computer attached to the machine.

Air-aging Study

Aging tests were performed in a multicell aging oven of Toyoseiki (Tokyo, Japan) at 150°C for 72 h. After completion of the tests, the samples were cooled at room temperature and the mechanical properties were measured, as described earlier.

Oil-swelling Test

Circular test pieces of radius 20 mm were die cut from the molded sheets. These were weighed ac-

curately and immersed in ASTM oil #3 at 150°C for 72 h. The specimens were removed from the oil, blotted, and weighed quickly in a glass-stoppered bottle. Volume swelling for the specimens was estimated as

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

where q is the ratio of swollen volume to original unswollen volume ($q - 1 = \%$ of the volume swell ÷ 100); W_1 and W_2, specimen weights before and after swelling, respectively; and ρ_c and ρ_s, the density of the composition and the oil, respectively. The density of the specimens (blends) varied from 1.10 to 1.12 g/cc (calculated on the basis of the volume fraction of plastic and rubber). The density of the ASTM oil #3 at 150°C measured using the standard procedure was 0.86 g/cc.

RESULTS AND DISCUSSION

Dynamic Mechanical Thermal Analysis (DMTA)

Figure 1 represents the DMTA results of ACM (crosslinked with 0.5 phr HMDC), PBT, and a 40/60 (w/w) blend of PBT and ACM (mix A_1) in terms of the temperature dependence of tan δ in the temperature range between −100 and 150°C. The spectra of ACM is shown in the log scale to show weak transitions at −35 and at −73°C. PBT
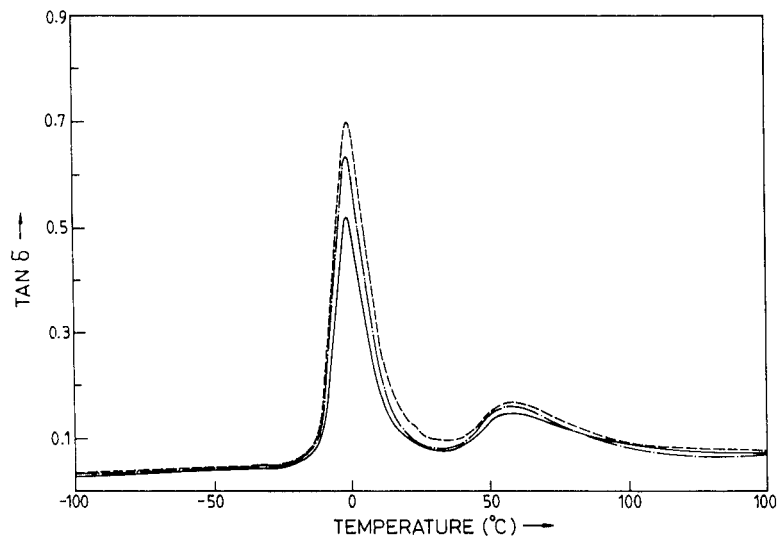
Figure 2 Temperature dependence of loss tangent (tan δ) of the blends at 10-Hz frequency: (——) A_1; (– · –) A_2; (- - -) A_3.

shows two loss peaks in the above temperature range which have been labeled α and β, occurring at 57 and $-58°C$, respectively. The α-peak is assigned to its T_g, which involves motion within the amorphous phase and is strongly dependent on the crystallinity of the material, while the β damping peak is attributed to the carboxyl group of the polyester forming H bonds.[10] In the case of ACM, three transitions are observed at 0, -35, and $-73°C$. The main transition at $0°C$ is ascribed to the glass–rubber transition or the T_g. The peak at $-35°C$ is due to the motion at the branch junction of ethyl ester side groups.[7] The 40/60 (w/w) PBT/ACM blend shows two main damping peaks, one at $-1°C$ corresponding to the glass transition of ACM and another peak at $54°C$ due to the T_g of the PBT phase. Although the peak positions are shifted compared to those of the homopolymers due to a small amount of phase-component miscibility between the blend components, the appearance of two separate tan δ peaks strongly suggests the microheterogeneity of the blend (i.e., two-phase morphological structure) and, hence, the incompatibility of the blend components.

The dynamic mechanical analysis of the mixes A_1, A_2, and A_3 are shown in Figures 2 and 3 in terms of temperature dependence of the loss tangent (tan δ) and storage modulus (E'), respectively. Figures 4 and 5 show the DMTA results of the mixes A_2C and A_2D, respectively, along with that of mix A_2 for comparison. It is clear from the loss tangent curves that all the blends show two

main transitions in the temperature range of -100 to $150°C$, one sharp peak near $0°C$ and other peak near $55°C$, corresponding to the glass transition temperatures of ACM and PBT, respectively, and confirming a two-phase morphology for the blends. The various parameters measured from the curves are shown in Table II. From the above figures and the table, the following changes are observed:

1. The tan δ_{max} corresponding to the glass transition of the rubber phase of the blends is increased with the progressive addition of ACM, although the T_g of ACM is unaffected in all the cases. However, the T_g and the tan δ_{max} corresponding to the PBT phase have not changed significantly with the addition of rubber.

2. The storage modulus (E') at $30°C$, which is characteristic of the stiffness of the blends at room temperature, decreases with increase in the ACM content in the blends. Also, the softest blend (A_3) shows a significant dynamic modulus at $150°C$ (3160 MPa), which suggests its applicability at that high service temperature range.

3. In the case of the 35/65 (w/w) PBT/ACM blend, which was melt-blended in the presence of the DBTDL catalyst, the glass-transition temperature of the ACM phase increases from 0 to $2°C$ with an increase in the tan δ_{max} value. Also, the storage modulus decreases at all temperatures com-
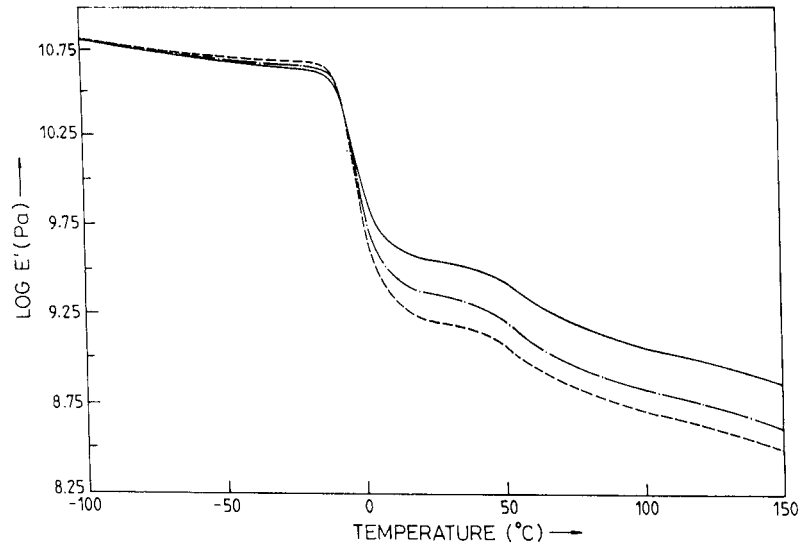
Figure 3 Temperature dependence of dynamic storage modulus (E') of the mixes at 10-Hz frequency: (—) A_1; (– · –) A_2; (- - -) A_3.

pared to that of the uncatalyzed blend. This may be explained on the basis of the interaction between PBT and ACM in the presence of DBTDL. The decrease of the storage modulus may be due to the probable reduction in the crystallinity of PBT due to interaction and also partial degradation of PBT in the presence of DBTDL.

4. An increase in the HMDC concentration during dynamic vulcanization of the 35/65 (w/w) PBT/ACM blend leads to a slight decrease in the storage modulus value at 30°C and an increase in the tan δ_{max} value of the rubber phase.

It is known that the height of the dynamic transition of a component of a composite apparently reflects the relative quantity of the compo-
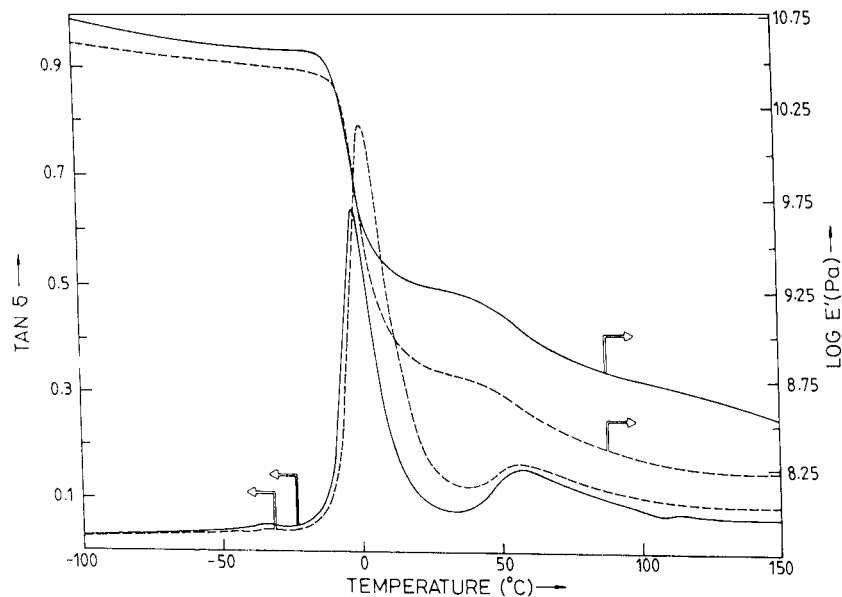

Figure 4 Temperature dependence of loss tangent (tan δ) and dynamic storage modulus (E') of the blends at 10-Hz frequency: (—) A_2; (- - -) A_2C.
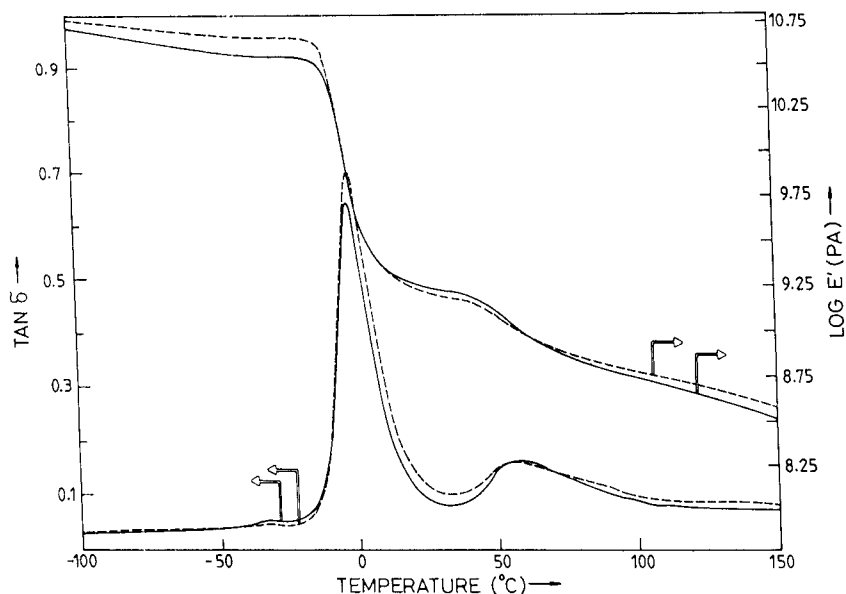
Figure 5 Temperature dependence of loss tangent (tan δ) and dynamic storage modulus (E′) of the blends at 10-Hz frequency: (——) A_2; (- - -) A_2D.

nent itself.[11–13] Also, the model calculation based on the modified Kerner's equation[11] indicates that the height of the dispersed-phase loss peak is principally a function of the inclusion volume fraction. This is reflected by the increase of the tan δ_{max} of the rubber phase with the increase in the relative amount of ACM in the blends, as described above. Also, the blends become softer with increase in the rubber-phase content. On the other hand, both the T_g and the tan δ_{max} corresponding to the PBT phase have changed marginally with the addition of ACM. PBT, being a semicrystalline polymer, has the glass transition tem-

Table II DMTA of the Blends

Mix No.	T_{g_r} [a] (°C)	tan δ_{max} [b]	T_{g_p} [c] (°C)	Log E' [d] (Pa)
PBT	—	—	57	9.77
ACM	−1	2.32	—	8.05
A_1	−1	0.53	54	9.58
A_2	0	0.65	56	9.26
A_3	0	0.72	57	9.18
A_2C	2	0.81	57	8.54
A_2D	0	0.71	56	9.22

[a] Glass transition temperature of the ACM phase.
[b] Tan δ value at the maximum peak position of the rubber phase.
[c] Glass transition temperature of the PBT phase.
[d] Storage modulus (log E') at 30°C.

perature of its amorphous phase controlled by the crystalline index of the polymer.[10] It is probable that in the case of a blend of PBT and ACM the marginal change in the T_g and tan δ_{max} values is due to the effect of ACM on the crystallization of PBT.

The most interesting result observed above is the change in the DMTA spectra of the 35/65 (w/w) PBT/ACM blend in the presence of 0.1% of DBTDL, which may be due to the occurrence of an transesterification reaction between PBT and ACM during melt blending in the presence of DBTDL. The same reaction could not be crosschecked with a control blend of PBT and ACM without any crosslinker, as it led to a soft and tacky mass after melt blending which could not be processed further. It is, however, known that two polyesters react to each other by the exchange of the ester groups at high temperature.[14–16] A similar reaction is also probable in the case of the above two polymers through ester group interchange, leading to PBT-g-ACM during the meltblending operation, which compatibilizes the two phases. As the ACM chains are grafted to the plastic matrix, its flexibility is reduced compared to the pure homopolymer. Also, the transreaction may lead to reduction in the crystallinity of the PBT phase and there is a possibility of partial degradation of the PBT phase in the presence of DBTDL. Unutilized DBTDL, if any, in a very

Table III   Mechanical Properties of PBT/ACM Blends

Mix No.	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore D)
A_1	10	66	44
A_2	7	75	42
A_3	5	89	38
A_2C	4	96	35
A_2D	8	67	42

minute quantity remaining in the mix after 5 min may react with HMDC and influence the crosslinking of ACM. The combined effect is reflected in the decrease of the storage modulus of the blend.

Mechanical Properties

The mechanical properties of the blends, that is, tensile strength, elongation at break, and hardness, are given in Table III. It is evident that with increase in the ACM content the rubbery properties of the blends are improved. The tensile strength and the hardness decrease and the elongation at break increases progressively. Similar results are also reflected in the dynamic mechanical properties of the blends, as discussed above. The blend with DBTDL shows the highest extensibility, which suggests the compatibilization of the blend components through a transesterification reaction in addition to partial loss of crystallinity, the reaction of unutilized DBTDL, if any, with HMDC, and partial degradation of PBT. The transesterification reaction during the melt-blending operation produces a PBT/ACM graft copolymer at the interface, which increases the adhesion between the two phases and thus improves the elongation-at-break value. The hardness of the transesterified blend is reduced because of the increased amorphous characteristics of the blends.

Heat and Oil Resistance

Table IV shows the mechanical properties of the blends before and after aging in air at 150°C for 72 h and the volume swell percentage in ASTM oil #3 at the same condition. As usual, the volume swell in ASTM oil #3 increases with increase in the rubber content in the blends. The blend A_2C shows the highest swelling due to minor reduction of the crystallinity, the reaction of residual

DBTDL, if any, with HMDC, and partial degradation of the PBT phase, which forms the main matrix. It may be pointed out that the two chemicals, DBTDL and HMDC, were added separately at two different stages during the mixing operation. DBTDL was added at $t = 0$ min and HMDC was added after 6 min of blending of PBT and ACM. It is expected that DBTDL would be consumed fully during 6 min to catalyze the transreaction between the two esters or to hydrolyze the esters partially. However, a very minute quantity of DBTDL, if any, remaining in the mix may react with HMDC and influence the crosslink density of ACM and, hence, the swelling. Also, with increase in the concentration of HMDC, the volume swelling of the blend (A_2D) decreases due to higher crosslink density of the ACM phase. However, it is clear from the above results that the volume swelling of the PBT/ACM blends in ASTM oil #3 at 150°C is well below 25%, which suggests its excellent hot-oil resistance. Coran and Patel[17] 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 blends.

The mechanical properties of the blends after air-aging at 150°C for 72 h suggest that, in most of the cases, the tensile strength and elongation at break increase with aging. It is probable that at 150°C the crosslink density of the ACM phase increases due to the postcuring reaction, leading to the improvement of the mechanical properties of the blends. The same trend is also observed in the case of hardness values.

Table IV   Heat and Oil Resistance of PBT/ACM Blends

Parameter	A_1	A_2	A_3	A_2C	A_2D
Oil aging at 150°C in ASTM oil #3					
Volume swell (%)	13	16	20	25	12
Aging at 150°C for 72 h					
Tensile strength (MPa)	12	8	9	4	11
Elongation at break (%)	78	90	94	70	67
Hardness (Shore A)	44	44	41	36	47

CONCLUSIONS

The dynamic vulcanization of PBT and ACM in an internal mixer like a Brabender Plasticorder in the temperature range of 220–230ºC presents a unique way of preparing novel heat- and oil-resistant thermoplastic elastomeric blends. The blend components were found to be incompatible in nature and exist as two separate phases, as evidenced from the DMTA results. The storage modulus (E') of the blends at 30°C, which is characteristic of the stiffness of the blends at room temperature, decreases with increase in the ACM content in the blends. Also, the softest blend shows a significant dynamic modulus at 150°C (3160 MPa), which suggests its applicability at that high service temperature range. The blend having DBTDL displays the highest elongation at break. An increase in the glass-transition temperature of the ACM phase (from 0 to 2°C) with an increase in the tan δ_{max} value support a probable transesterification reaction between the components. The mechanical properties are a function of the blend components, amount of crosslinker, and interaction between PBT/ACM. The blends show excellent resistance to oil swelling at elevated temperature (e.g., 150ºC) and its service temperature range can be extended to 150ºC without much deterioration of the mechanical properties The volume swell in ASTM oil #3 at 150ºC of the blends is well below 25%, which suggests its excellent hot-oil resistance.

REFERENCES

1. Coran, A. Y. In Handbook of Elastomers—New Developments and Technology; Bhowmick, A. K.; Stephens, H. L., Eds.; Marcel Dekker: New York, 1988; Chapter 8.
2. Rader, C. P.; Abdou-Sabet S. In Thermoplastic Elastomers from Rubber–Plastic Blends; De, S. K.; Bhowmick, A. K., Eds.; Ellis Horwood: London, 1990; Chapter 6.
3. Wolfe, J. R. In Thermoplastic Elastomers—A Comprehensive Review; Legge, N. R.; Holden, G.; Schroeder, H. E.; Eds.; Hanser: New York, 1987; Chapter 6.
4. Coran, A. Y. In Thermoplastic Elastomers—A Comprehensive Review; Legge, N. R.; Holden, G.; Schroeder, H. E.; Eds.; Hanser: New York, 1987; Chapter 7.
5. Venkataswamy, K. In Symposium on Dynamic Vulcanizates, Polymeric Materials Science and Engineering Division, Fall ACS Meeting, Boston, 1998.
6. Venkataswamy, K.; Payne, M. T. In Symposium on TPE, ANTEC, Dallas, TX, 1990.
7. Jha, A.; Bhowmick, A. K. Rubber Chem Technol 1997, 70, 798.
8. Jha, A.; Bhattacharyya, A. K.; Bhowmick, A. K. Polym Networks Blends 1997, 7, 177.
9. Jha, A.; Bhowmick, A. K. J Appl Polym Sci 1998, 69, 2337.
10. Murayama, T. In Encyclopedia of Polymer Science and Engineering; Mark, H.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1990; Vol. 5, pp 299–329.
11. Dickie, R. A. In Polymer Blends; Paul, D. R.; Newman, S., Eds.; Academic: New York, 1978; Vol. I.
12. Nielsen, L. E. Mechanical Properties of Polymers and Composites; Marcel Dekker: New York, 1974.
13. Manson, J. A.; Sperling, L. H. Polymer Blends and Composites; Plenum: New York, 1976.
14. Porter, R. S.; Wang, L. H. Polymer 1992, 33, 2019.
15. Kotliar, A. M. J Polym Sci Macromol Rev 1981, 16, 367.
16. Jha, A.; Bhowmick, A. K. Polymer 1997, 38, 4337.
17. Coran, A. Y.; Patel, R. Rubber Chem Technol 1983, 56, 1045.