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Thermoplastic elastomeric blends of poly(ethylene terephthalate) and acrylate rubber: 1. Influence of interaction on thermal, dynamic mechanical and tensile properties

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Poly(ethylene terephthalate) (PET) and acrylate rubber (ACM) were solution blended in nitrobenzene, a common solvent, at 160°C. The blend film (50/50 weight ratio) was heated at 300°C for different times to induce *trans*-esterification reaction between the two components and the extent of the reaction was characterized by i.r. spectroscopy. The effects of the reaction on the thermal, dynamic mechanical and tensile properties of the blends were studied. The results confirm the possibility of *trans*-reaction between PET and ACM components at 300°C up to 45 min, after which the degradation of the phases is predominant. Better mechanical properties support the *in situ* compatibilization of the two phases via *trans*-reaction, which increases the adhesion between the two components at interface. © 1997 Elsevier Science Ltd.

(Keywords: thermoplastic elastomer; polymer blend; compatibilization; *trans*-esterification; acrylic rubber; polyethylene terephthalate)

INTRODUCTION

Thermoplastic elastomers have the ease of processing like thermoplastic and behave like a crosslinked rubber under ambient conditions. There are five classes of thermoplastic elastomers, out of which the ones prepared from the blends of rubber and plastics have gained popularity in recent years. The blends are cheap and the properties could be monitored by simple means like variations of the blend ratio, the viscosity of the components, and incorporation of additives or cross-linking agents. However, the concept of thermoplastic processing is anti-thetical to the performance and the stability at high temperature. Most of the thermoplastic elastomers prepared so far have poor high temperature properties. For example, commercial blends like ethylene-propylene diene (EPDM)–polypropylene (PP), nitrile rubber (NBR)–polypropylene (PP), natural rubber (NR)–polypropylene (PP), etc. have a maximum operating temperature of 160°C. Coran[1] reported that the thermoplastic elastomers could be made by using plastic of high melting point and thereby the operating temperature may be enhanced. However, many of the plastics like polyamide present some interesting processing problems, somewhat like those involved in perfluoro carbon resins[2]. Also many high temperature rubbers like silicones, which can withstand high temperature, do not have appropriate match of hard segments. The problems are still aggravated when chemical resistance is demanded from such thermoplastic elastomers. It is

with this background that the present investigation has been initiated. The objective of our programme is to develop a series of novel heat and oil resistant thermoplastic elastomers based on blends of rubber and plastics. In this paper, we report our observation on the blends of poly(ethylene terephthalate) (PET) and acrylic elastomer with special reference to the interaction between the components. The ester groups of acrylate rubber and the terminal hydroxyl groups of PET are the potential reactive sites for *trans*-esterification[3]. The reactive compatibilization via *trans*-reaction was reported by several authors[4–6]. In our earlier work, we have highlighted the influence of interaction on the properties of rubber–plastics[7–10] and rubber–rubber blends[11]. Such studies are required to optimize composition and properties of any blend.

EXPERIMENTAL

Materials

PET polyester Arnite A02-300 in pellet form (intrinsic viscosity = 0.72 dl g^{-1}) was supplied by Akzo Plastics, Netherlands. Acrylic rubber (ACM) JSR AR 102X was obtained from Japan Synthetic Rubber Company Limited, Tokyo, Japan. It was reported to have double bond cure site and made from ethyl acrylate monomer.

Blending

PET and ACM were dried at 120°C for 24 h and at 80°C for 16 h respectively *in vacuo*, prior to blending. The blends were prepared in batches of 2 ± 0.2 g polymer in

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nitrobenzene solvent. The rubber was dissolved in nitrobenzene at room temperature with occasional stirring for 3 days to get a homogeneous solution of 2% by weight. PET was dissolved in nitrobenzene at 160°C for 30 min to form a solution with concentration 2 g per 100 ml of the solvent. The rubber solution was then added to it with constant stirring. The mixture was stirred continuously for 30 min and the temperature of the mixture was kept at 160 ± 2°C. The blend was then drip precipitated from cold petroleum ether with stirring. The ratio of the petroleum ether to nitrobenzene was kept at 7:1. The precipitated polymer was filtered and washed 4–5 times with petroleum ether to remove the nitrobenzene. It was then dried at 100°C for 24 h *in vacuo*.

Sample preparation

The compositions prepared under these conditions were 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100 PET/ACM (w/w). The films were prepared by compression moulding between two teflon sheets at 300°C and 10 MPa pressure for different times in a hydraulic press. After releasing the pressure, the samples were quenched at room temperature. The resulting film thickness was 0.6–0.8 mm.

I.r. spectroscopy

PET/ACM blend at 50/50 weight ratio was dissolved in nitrobenzene at 160°C to prepare a solution at a concentration of 1 g/100 ml. One drop of this hot solution was spread on KBr disc and the solvent was evaporated at 120°C under high vacuum for 24 h. I.r. spectra showed no changes in the carbonyl peak intensity of the ester groups before and after heating at 120°C for 24 h, thereby confirming that no degradation of the ester links of both the acrylates and terephthalates took place during this operation. A Perkin–Elmer Spectrophotometer, model 843, was used for the i.r. analysis. The samples were scanned from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 3.2 cm^{-1} and four scans were averaged for each spectra. For studying the extent of *trans*-esterification reaction between PET and ACM, the KBr disc with the blend film on it was heated at 300°C for different times inside a sealed aluminium block. The spectra were then taken at room temperature under identical conditions stated above.

Dynamic mechanical thermal analysis

Dynamic mechanical analysis of the blends and the individual polymers were performed on a DMTA Rheometric Scientific MK-II model in bending dual-cantilever mode. The experiments were carried out at three frequencies, e.g. 1, 10 and 100 Hz at a heating rate of 2°C min^{-1} and a double strain amplitude of 64 μm over a temperature range of −50°C to 200°C. The storage modulus, E', loss modulus, E'' and loss tangent, tan δ were measured for each sample in this temperature range. The samples (36 mm × 12 mm × 0.8 mm) were cut from the blend films.

Thermal analysis

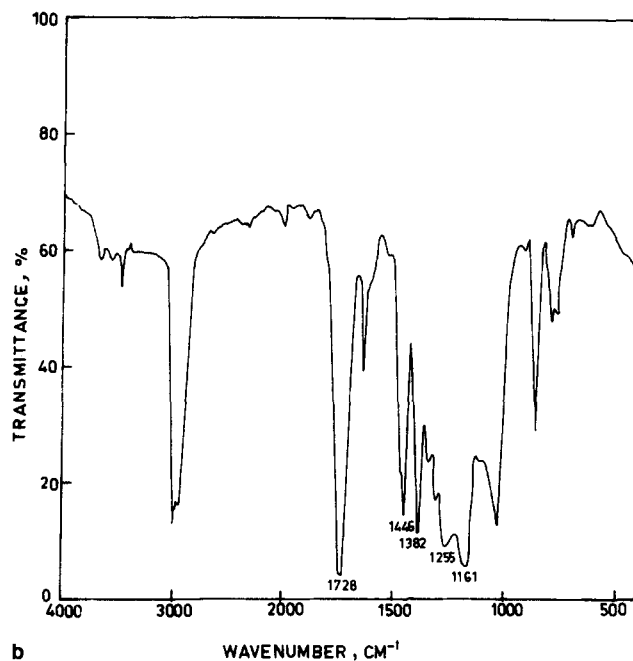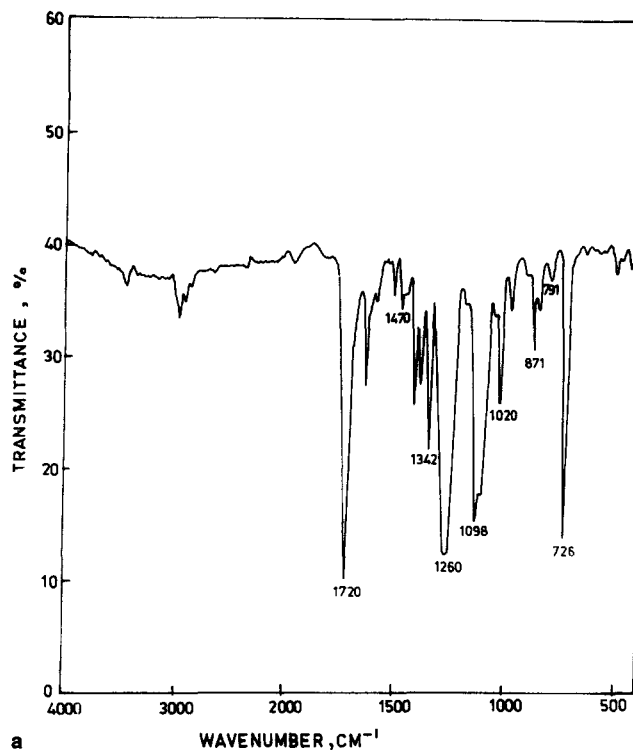The thermal analysis was carried out using DuPont 9000 Thermal Analyser at a heating rate of 20°C min^{-1}.

Figure 1 I.r. spectra of solution cast film of (a) poly(ethylene terephthalate) (PET), (b) acrylate rubber (ACM)

The samples (∼10 mg), sealed under aluminium pans were scanned from −100°C to 500°C under a nitrogen blanket with a flow rate of 40 ml min^{-1}. The results reported here were the average of three samples. T_m and ΔH were reproducible within ±1°C and ±5% respectively.

X-ray measurements

X-ray diffraction profiles were recorded using CuK_α radiation using a Philips X-ray diffractometer (Philips PW-1840 diffractometer). The diffractograms were analysed by standard methods[12]. The degree of crystallinity was determined from the ratio of the areas under the crystalline peaks and the amorphous halo. The errors in

Table 1 Assignment of i.r. bands of (a) poly(ethylene terephthalate) and (b) acrylate rubber

Wave number, cm^{-1}	Assignment
(a) Poly(ethylene terephthalate)	
1720	>C=O stretching of the terephthalate unit
1470	CH_2 bending of ethylene unit
1342	CH_2 wagging
1260	C–O–C assym. stretching
1098	C–O–C sym. stretching
1020, 871, 726	Aromatic ring
791	C–H bending of terephthalate unit
(b) Acrylate rubber	
1728	>C=O stretching of the acrylate ester unit
1446	CH_3 assym. deformation
1382	Sym. CH_3 deformation
1255	C–O–C assym. stretching
1161	C–O–C sym. stretching.

peak angle and percentage crystallinity were ±0.1 and ±2% respectively.

Tensile testing

Tensile tests were performed according to ASTM D 412-80 test method using dumb-bell shaped test pieces which were punched out from the moulded films using BS-E-type die. The tests were carried out in a Zwick Universal Testing Machine (UTM) model 1445, at $25 \pm 2°C$ and a cross-head speed of $500\,mm\,min^{-1}$ with a gauge length of 34 mm. The modulus and the tensile strength are reported in MPa. The experimental error was ±5%.

RESULTS AND DISCUSSION

I.r. analysis

The i.r. spectra of solution cast films of PET and ACM are shown in *Figures 1a* and *1b* respectively and the characteristic peaks are assigned accordingly (*Table 1*). The C–H bending of the terephthalic unit at 791 cm^{-1} is used as an internal standard[13] during the analysis of the difference spectra.

The *trans*-esterification reactions between the two esters are not unambiguous since both the reactants and the products belong to the same class of compounds. The carbonyl stretching frequencies of the ester groups of both PET (at 1720 cm^{-1}) and ACM (at 1728 cm^{-1}) are very close to each other and overlap to form a single band in the same region (*Figure 2*). Hence, the detection of >C=O stretching frequency of the mixed ester produced by *trans*-esterification reaction is also impossible due to the overlapping of the bands in the same region. However, the symmetric stretching frequencies of C–O–C bonds of both lie in two different regions (1098 cm^{-1} for PET and 1161 cm^{-1} for ACM) and any chemical reaction between these functional groups must produce some changes in the intensity of these two peaks or generate some new peaks characteristic of the mixed ester in between these two regions. In fact, a new peak at 1134 cm^{-1} is observed in the difference spectra when the blend is heated at 300°C for different times (*Figure 3*). With the increasing time of heating (i.e. with the advancement of the *trans*-esterification reaction) the peak height increases gradually up to 45 min of heating and remains unchanged after further heating. This is also followed by a gradual reduction in the height of the peak
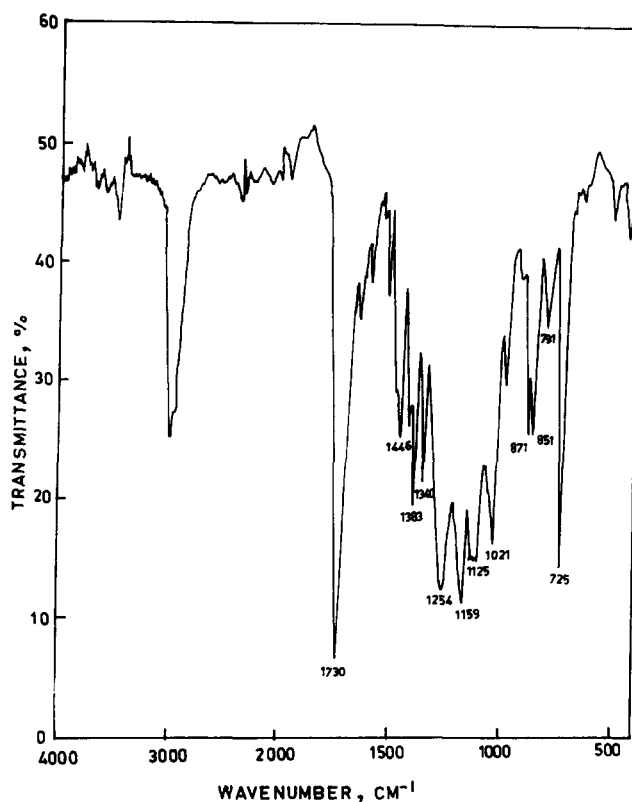

Figure 2 I.r. spectra of 50/50 weight ratio blend of PET and ACM

at 1158 cm^{-1} (which is a characteristic peak of the C–O–C stretching frequency of ACM ester unit) with the advancement of the reaction. Hence, from the i.r. analysis, we infer that a reaction similar to the *trans*-esterification
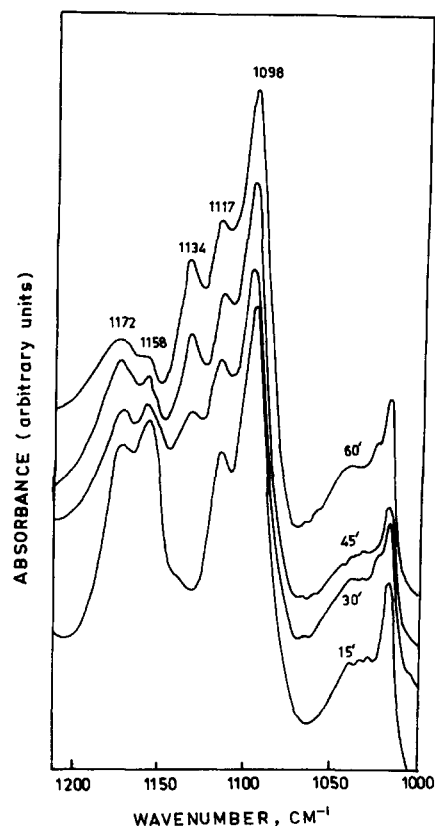

Figure 3 Difference spectra of 50/50 (w/w) blends reacted for different times from the control (peak at 791 cm^{-1} of PET is taken as reference)

Table 2 Thermal properties of PET–ACM blends

Blend (PET/ACM, w/w)	T_g (°C) PET	T_g (°C) ACM	$T_m{}^a$ (°C) PET	PET[b] crystallinity (%)
100/0	76	—	253	26
80/20	76	−20.0	253	32
60/40	76	−17.0	255	22
50/50	76	−13.0	255	33
40/60	—	−15.5	253	45
20/80	—	−16.5	255	41
0/100	—	−13.6	—	—

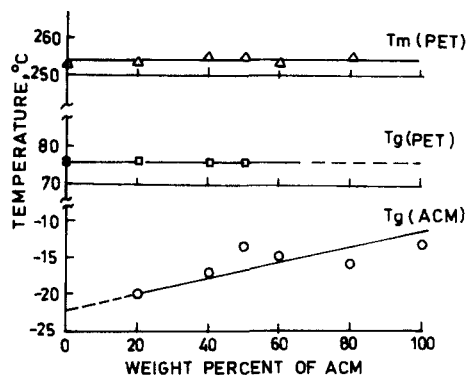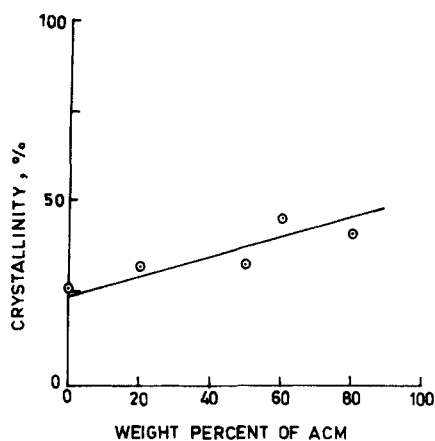[a] Temperature (peak minimum)
[b] ΔH_f (PET) $= 1.4 \times 10^5$ J kg^{-1}

Figure 4 Phase diagram of PET/ACM blends, without *trans*-esterification

**Figure 5** Composition vs fractional PET crystallinity from d.s.c. data

Table 3 Effect of heating on the thermal properties of 50/50 (PET/ACM) blend

Heating time (min) at 300°C	T_g (°C) PET	T_g (°C) ACM	T_m (°C) PET	T_c (°C) PET	Area under T_c (arbitrary value)
15	74.0	−14	257	119	246
30	73.3	−15	254	116	248
45	71.5	−15	257	115	270
60	72.6	−15	257	115	135

between PET and ACM component can occur at high temperature (i.e. at 300°C). However, the i.r. analysis of pure PET and ACM does not show any change in their spectral behaviour when heated at 300°C for similar times.

Thermal properties of the blends

Table 2 and Figure 4 summarize the thermal analysis
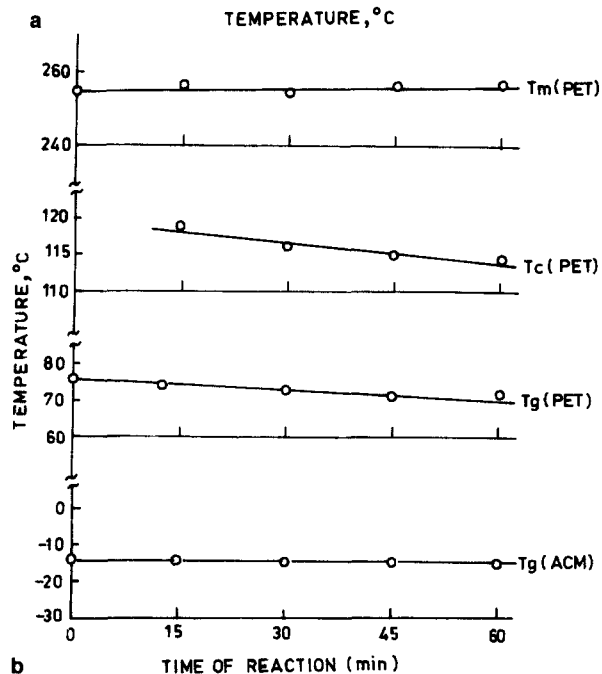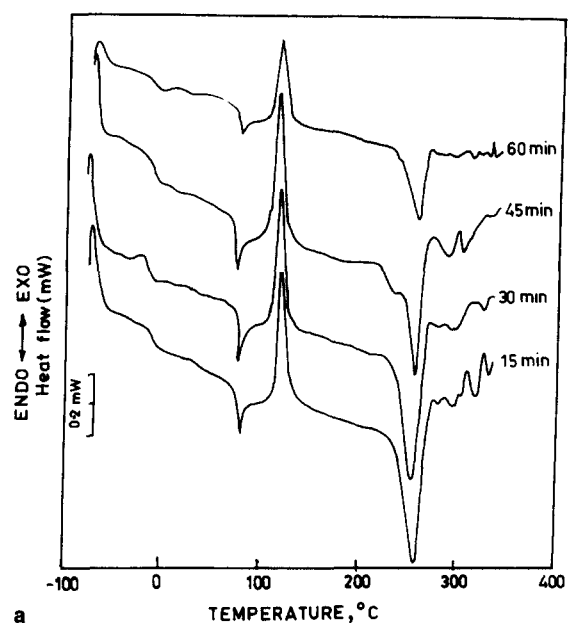
Figure 6 (a) D.s.c. thermograms of 50 PET/50 ACM (w/w) blends with different *trans*-esterification times at 300°C. (b) Transition temperatures of 50 PET/50 ACM (w/w) blends at different reaction times at 300°C

data of PET/ACM blends of different compositions. The percentage crystallinity of PET component is calculated assuming a heat of fusion of PET crystal of 1.4×10^5 J kg^{-1} [14].

The above results show that both the T_g and the T_m of PET are unaffected by the presence of ACM at all proportions. The T_g of ACM is, however, decreased progressively with the addition of PET in the blend. It is suggested that low molecular weight PET fractions can act as a plasticizer for ACM molecules and thereby increase the flexibility of the chains, which results in the reduction of the glass transition temperature (*Figure 4*).

The crystallinity of the PET component, as determined from the heat of fusion of PET, normalized for fractional content is shown in *Figure 5* and *Table 2*, where additional data on thermal transitions are recorded. *Figure 5* shows that the crystallinity of the PET in the blend is enhanced in the presence of the acrylate elastomer. It is reported[15] that poly(methyl methacrylate) facilitates crystallization of

PET. This indicates that the presence of acrylate elastomer component enhances the formation and nucleation of PET crystals, thereby increasing its crystallinity. This is another indication of strong interface interactions between the components which modify crystal perfection and purity.

The effect of heating of 50/50 blends at 300°C for different times and subsequent quenching to room temperature on the thermal properties of the blend are shown in *Table 3* and *Figure 6*. It is clear from *Figure 6* that both T_g and T_c of PET are reduced progressively with the advent of the reaction, although the T_m of PET is almost unaffected with the reaction time. The same trend is also observed for T_g value of ACM. This indicates a strong interaction between the phases of PET and ACM, probably through the *trans*-esterification reaction between the two components at 300°C. It is plausible that the polymer blend suitably reacts to form block copolymer and finally random copolymer[3]. Formation of such product at the interface may enhance the miscibility of the blend components, thereby affecting the glass transition temperature of the respective components. This effect is reflected in the area under cold crystallization curve (from 115°C to 119°C) which is found to be increased with time. This area reaches a maximum value at 45 min and then reduces with further time. The abrupt decrease in the area under both PET crystallization and PET melting peak after 45 min is probably caused by the degradation of PET phase on prolonged heating at that high temperature. X-ray data reported in *Table 4* corroborate the above observations, although the values of crystallinity are a little higher. Also, new peaks at around 9° and 6° appear on heating the blends at different times.

Dynamic mechanical thermal analysis

The results of dynamic mechanical thermal analysis are plotted in *Figure 7* in terms of the temperature dependence of storage (E') modulus and tan δ for the 50/50 (w/w) blend of PET and ACM. The glass transition temperature is selected as the peak position of the tan δ when plotted against temperature.

Pure ACM exhibits transitions at 0°C, which can be attributed to the glass transition temperature. The T_g of pure PET is detected at 93°C. As expected, these transitions occur at higher temperatures as compared to those obtained in d.s.c. measurements. The 50/50 blend without interaction shows two transitions at 0°C and at 93°C, indicating a two phase morphological structure of the blend. The same blend was heated at 300°C for different times and quenched at room temperature. The variations of $\log E'$ and tan δ with temperature are shown in *Figures 8* and *9* respectively. The *trans*-esterification reactions between the ACM and the PET phases, as inferred from the i.r. and thermal analysis, also affect the dynamic mechanical properties of the blend. The T_g of the rubber phase is shifted to 4°C and this position is unaffected with the increase in the time of the reaction. The peak corresponding to the T_g of plastic phase in the tan δ vs temperature plot is split into two parts: one at around 80°C and another at 100°C (*Figure 9*). As the heating time is increased, the peaks both at 80°C and 100°C are shifted progressively towards lower temperature up to 45 min of heating and then shifted towards the original position. The same observation is made with the 60:40 blends. The control sample (i.e. without heating) and the blend heated at 300°C for 1 h display the same trend (*Figure 10*).

The formation of a new tan δ peak near 100°C can be attributed to the crystallization of PET phase which is also reflected in the increase of storage modulus of the

Table 4 X-ray properties of PET/ACM (50/50) blends: *trans*-esterification for different times at 300°C

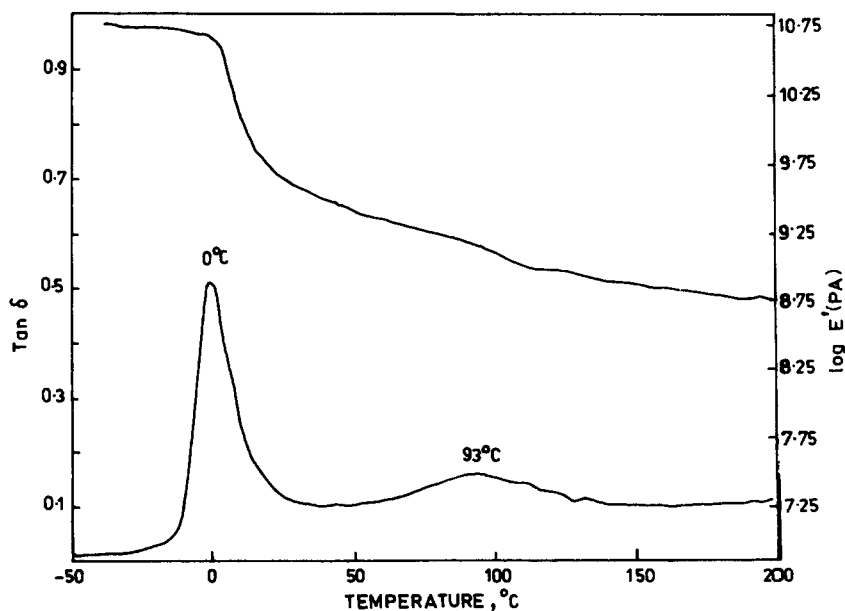| Time of reaction (min)	2θ values	Crystallinity (%)
15	23°, 26.2°	29.1
30	22.6°, 26.4°, 18°, 12°	36.0
45	23.5°, 26.3°, 18°, 12.7°	37.4
60	22.8°, 24.4°, 17.2°, 10.8°	34.5

Figure 7 Dynamic mechanical properties of 50 PET/50 ACM blends as a function of temperature, without *trans*-esterification
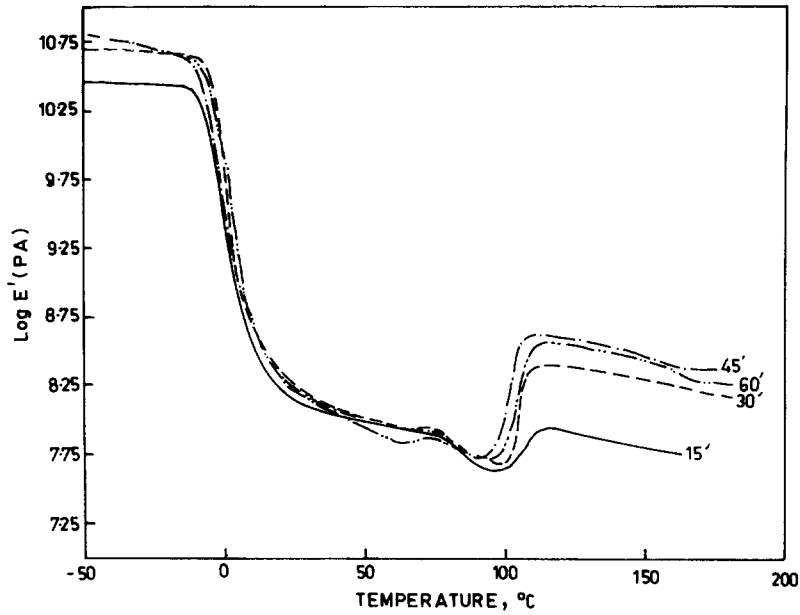
Figure 8 Temperature dependence of storage modulus (E') of PET/ACM (50/50) blends heated at 300°C for different times
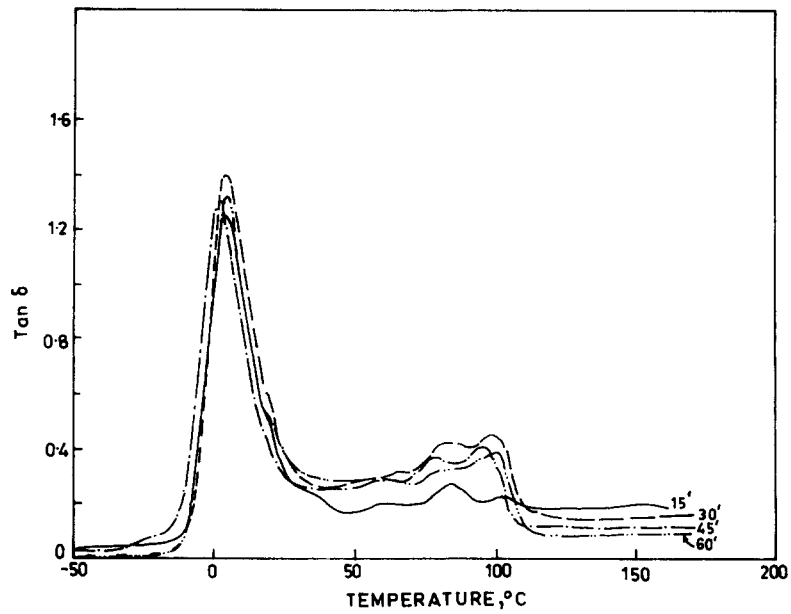

Figure 9 Temperature dependence of dynamic mechanical loss (tan δ) of PET/ACM (50/50) blends heated at 300°C for different times
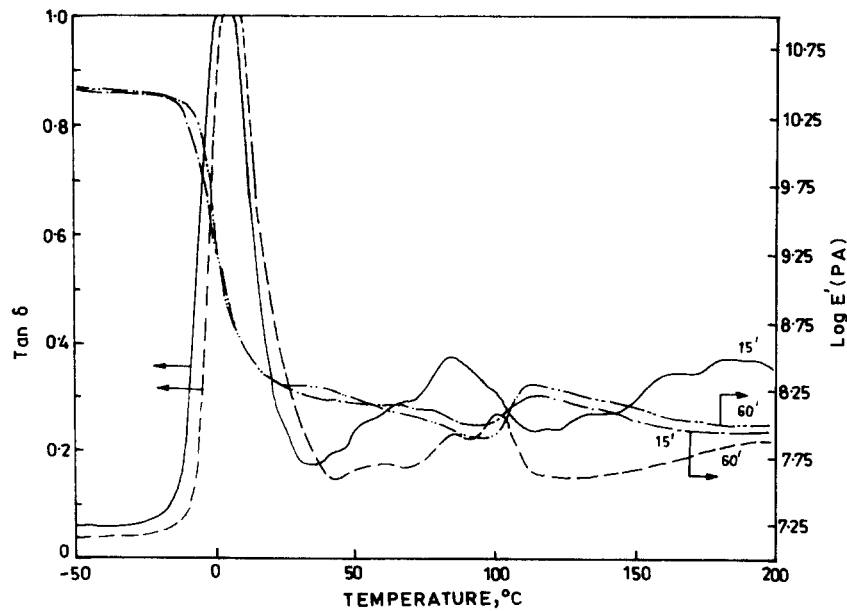

Figure 10 Dynamic mechanical properties of PET/ACM (40/60) blends heated at 300°C for 15 and 60 min

blend around 110°C (*Figure 8*). It is interesting to note that the modulus value around 110°C gradually increases up to a time of 45 min heating and then marginally decreases. This also implies the gradual increase of the percent crystallinity of the blend during heating up to 45 min. These results are in accord with the studies using d.s.c.

Tensile properties

The stress–strain behaviour of the 50/50 PET/ACM blend is given in *Figure 11*. It is clearly found that with the increase in the time of heating, the tensile strength and the modulus increase with a progressive decrease in the strain at break (*Table 5*). When the corresponding compounds are annealed at 100°C for 2 h to initiate the crystallization of the plastic phase, the modulus values are all increased. These changes are more prominent in the 60/40 ACM/PET blend. When the tensile specimens are annealed at 300°C for 1 h, the modulus and the tensile strength are increased many fold with no change in the strain at break value as compared to those heated for 15 min at the same temperature (*Figure 12*).

The enhanced tensile strength and the modulus values are due to the formation of a block or random copolymer of PET and ACM at the interface during heating which acts as compatibilizing agent between the rubber and the
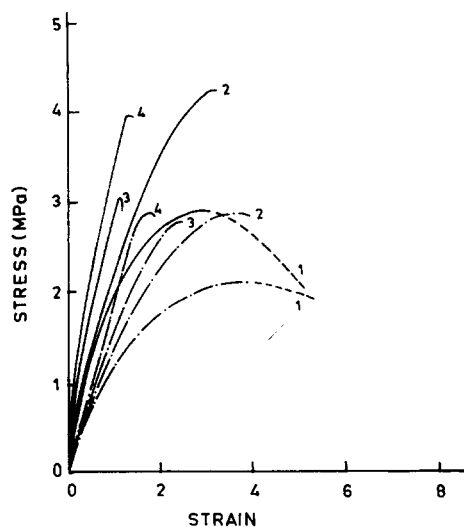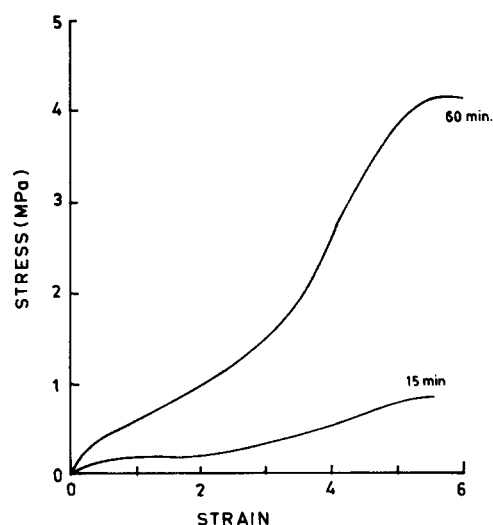

Figure 12 Stress–strain behaviour of 40 PET/60 ACM blend, *trans*-esterified at 300°C for 15 and 60 min

plastic phases and enhances the adhesion between the two.

CONCLUSIONS

PET and ACM are solution blended at 160°C in nitrobenzene and reprecipitated in petroleum ether at room temperature. The blend film (50/50 weight ratio) was heated at 300°C for different times to induce *trans*-reaction between the two components.

1. I.r. analysis indicates the formation of a new peak at 1134 cm^{-1} confirming the *trans*-esterification reaction between PET and ACM at 300°C.
2. D.s.c. and X-ray analysis show that the presence of ACM increases the total blend crystallinity, both in *trans*-esterified and without *trans*-esterified blend.
3. A strong interaction between PET and ACM phases at high temperature is also revealed from the d.m.t.a. studies. This lowers the T_g of the plastic phase significantly from 93°C to 80°C. Also, a new peak around 110°C in the $\tan \delta$ vs temperature plot indicates the crystallization of the PET phase.
4. The increase in the tensile strength (e.g. from 2.1 MPa to 2.8 MPa) and in the 200% modulus values (from 1.72 MPa to 2.9 MPa) indicates a strong interfacial adhesion due to *trans*-esterification reaction. This is also revealed in the mechanical properties of 60/40 ACM/PET (w/w) blend where the tensile strength is

Figure 11 Stress–strain properties of 50 PET/50 ACM blends, *trans*-esterified at 300°C for different times. (1) 15 min, (2) 30 min, (3) 45 min, (4) 60 min; (1)–(4) all annealed at 100°C for 2 h (solid lines for annealed samples)

Table 5 Mechanical properties of 50/50 (PET/ACM) blends

Sample number	Description	100% modulus	200% modulus	300% modulus	Tensile strength (MPa)	Strain at break
1	Heated at 300°C for 15 min	1.22 (2.0)	1.72 (2.71)	2.03 (2.9)	2.1 (2.9)	3.9
2	Heated at 300°C for 30 min	1.34 (2.24)	2.23 (3.47)	2.77 (4.23)	2.9 (4.3)	3.6
3	Heated at 300°C for 45 min	1.47 (2.24)	2.6 (—)	— (—)	2.8 (3.1)	2.4
4	Heated at 300°C for 60 min	1.89 (3.24)	2.9 (—)	— (—)	2.0 (4.0)	1.9

The values in parentheses indicate the properties of the sample after annealing at 100°C for 2 h

increased five times from that of the original value, when heated at 300°C for 60 min.

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