

Rheology and Transesterification between Polycarbonate and Polyesters

Sanket Nabar, D. D. Kale*

Department of Paint Technology and Polymer Technology, Mumbai University Institute of Chemical Technology, Matunga, Mumbai 400 019, India

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ABSTRACT: Rheological behavior of polycarbonate (PC)–polyester blends is studied. The miscibility and rheological behavior are discussed. Effect of catalyst, tetra-*n*-butyl orthotitanate on the transesterification reactions for a [60 (PC):40 (PET or PBT)] blend is studied rheologically. The blends were mixed for different spans of time for rheological study. The blends are analyzed on the basis of the mechanism sug-

gested by other researchers. As the mixing time is increased, the blends show decrease in viscosity. Random copolymers also are amorphous in nature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2039–2047, 2007

Key words: miscibility; blending; rheology; polyesters; differential scanning calorimetry (DSC)

INTRODUCTION

Blends of polycarbonate (PC) with polyesters exhibit some unique features. Most of the research work reported in the literature is devoted towards miscibility and transesterification reactions between PC and poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT).^{1–32} The miscibility between PC and polyesters has been attributed to possible transesterification reactions.

Solution cast blends of PC and PET or PC and PBT are found to form nonmiscible blends by many researchers.^{1–7} Hobbs et al.³ who studied solution blending as well as melt blending have shown that melt blending of PC with PBT formed partially miscible system. Melt blending of PC with PET/PBT has also received attention of many.^{8–15} Devanux and coworkers^{16–20} in their series of papers have studied possible exchange reactions, structures of possible copolyesters, and kinetic studies of the possible reactions in PC-PBT and PC-PET blends. They prepared the melt blends and evaluated the blends by IR and NMR techniques. They observed that as the reaction proceeded, a soluble random copolycondensate was progressively formed. They concluded that the most likely mechanism taking place in the blend was a reversible direct transesterification catalyzed by Ti resi-

due present in commercial PBT. The rate constants of forward and reverse reactions were identical. They also observed that the butylene carbonate formed in the system was much more stable than ethylene carbonate.

Berti et al.^{21,22} studied the different reactions that take place in melt blending of PC-PET in presence of titanium tetrabutoxide, Ti(OBu)₄, as a catalyst that is effective in promoting ester/carbonate exchange reactions. They found the formation of volatile cyclic ethz elimination of ethylene carbonate introduced strong changes in the resulting chemical structure. Ma et al.²³ used random copolymer of PC-PET blend (50/50, wt %) as the compatibilizer for PC-PET blend. They observed that more than 60 wt % of copolyester was required to obtain the single *T_g* in PC-PET blend. Wilkinson et al.²⁴ prepared PC-PBT blend by adding alkyl titanium as transesterification catalyst. They observed that as the degree of transesterification increased, the blend changed its nature from block copolymer to random copolymer. They observed the changes in morphology of the blend from coarse bicontinuous to finer bicontinuous dispersion as the degree of transesterification increased.

Fiorini et al.^{25,26} studied the effects of various catalysts on the reactive blending of PC-PET blends. They found that Ti(OBu)₄ that acts as a catalyst had the highest activity among all the catalysts. They found that Ti catalyst yielded fast reactions as compared to Tin catalyst but at the same time, side reactions took place, leading to discoloration and gas evolution that was not observed to significant extent for Sb catalyst. They observed that lanthanide series catalysts were more active for exchange reactions but did not cata-

Correspondence to: D. D. Kale (ddkale@gmail.com).

*Present address: Reliance Industries Ltd., PARC, Swastik Mill Compound, V. N. Purav Marg, Chembur, Mumbai 4000071, India.

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lyze side reactions. Ignatov et al.^{27–29} prepared PC-PET blends using different catalysts that were freshly added. They found that freshly added catalyst were more effective than residual catalyst and the contribution of side reactions such as degradation of carbonate group, release of CO₂, and cyclic ethylene carbonate was much less in lanthanide catalyst as compared to Ti catalyst. Wilkinson et al.³⁰ prepared PC-PBT blend with adding alkyl titanium as transesterification catalyst. As the degree of transesterification increased the blend changed its nature from block copolymer to random copolymer. As the degree of transesterification increased a progressive reduction in the degree of crystallinity, melting temperature, and crystallization temperature was observed. They observed a mixed phase T_g about 90°C, which agreed with the value predicted by Fox equation (86°C). Devanux and Godard^{31,32} studied the kinetic aspects of exchange reactions in PC-PBT blends as a function of temperature and PC/PBT ratio.

It is clear from above literature that extent of transesterification reactions are strongly influenced by catalyst and reaction conditions. The effect of extent of reactions for different mixing times on rheology of resulting blend has not received any attention. Present work aims at rheological behavior of melt blended PC-PBT and PC-PET blends for different mixing times.

EXPERIMENTAL

Materials

Commercial grades of bisphenol-A polycarbonate [CALIBRE Grade T-303 (Dow Chemicals)], PET [RELPE, Grade G5801, I.V. 0.80 dL/g (Reliance Industries, Mumbai, India)], and PBT [LUPOX, GP-1000, I.V. 1.00 dL/g (LG Polymers India Pvt)] were used. Tetra-*n*-butyl orthotitanate (TBOT; Merck) was purchased from local market.

Drying

Prior to blending, PC, PET, and PBT pellets were dried at 115°C ± 5°C for 4–5 h in an air-circulating oven. The drying is essential to remove the moisture absorbed by the materials.

Melt blending

The blends of PC-PET (60 : 40 w/w) and PC-PBT (60 : 40 w/w) were prepared using counter rotating twin screw extruder. The temperature profile was 220, 235, 250, and 260°C (Die). The extrudate strands were palletized and these pellets were denoted as 0 min mixture and used as the starting material for the further experiments. This is essential to avoid batch to

TABLE I
Blend Compositions Studied in Present Work

PC-PET blends	
Batch 1	0 min, no catalyst
Batch 2	2 min, 0.1 catalyst
Batch 3	4 min, 0.1 catalyst
Batch 4	15 min, 0.1 catalyst
Batch 5	15 min, no catalyst
PC-PBT blends	
Batch 6	0 min, no catalyst
Batch 7	2 min, 0.1 catalyst
Batch 8	4 min, 0.1 catalyst
Batch 9	8 min, 0.1 catalyst
Batch 10	15 min, 0.1 catalyst
Batch 11	15 min, 0.2 catalyst
Batch 12	15 min, no catalyst

batch variation. The dried pellets were melt mixed in a batch mixer (Haake Rheochord) with TBOT as catalyst for possible transesterification for different mixing times. The temperature of 260°C and rotor speed of 60 rpm was employed. The different compositions of blends studied are given in Table I. The resultant lump from batch mixer was compression molded into sheets at 280°C using Sterling Hydraulic compression molding machine. The dimension of the sheet is 15 cm × 15 cm × 2 mm (length × breadth × thickness).

Rheological properties

The melt viscosity was measured using rotational rheometer [RT 10, Haake Germany]. The samples were predried before analysis. Both constant shear stress and oscillatory modes were used for rheological study using parallel plate assembly. A sensor has diameter of 35 mm.

Melt viscosity η (Pa s) as a function of shear rate, $\dot{\gamma}$ (1/s), and the dynamic properties, i.e., storage modulus G' (Pa), loss modulus G'' (Pa), and phase angle $\tan \delta = G''/G'$ as a function of frequency ω (rad/s) were measured. The shear rate range was varied from 0.01 to 100 s⁻¹ and similarly the frequency of oscillation was varied from 0.1 to 40 Hz.

Differential scanning calorimeter (DSC)

Glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c) of all the blends as well as virgin polymers were studied using DSC-7 (Perkin-Elmer, USA). Temperature calibration was performed using Indium as a reference ($T_m = 156.60^\circ\text{C}$ and heat flow = 28.5 J/g). The heating rate of the samples was 20°C/min with a sample size between 7 and 13 mg using standard aluminum sample pan. The experiments were carried out under nitrogen atmosphere. For all the schemes same method was used.

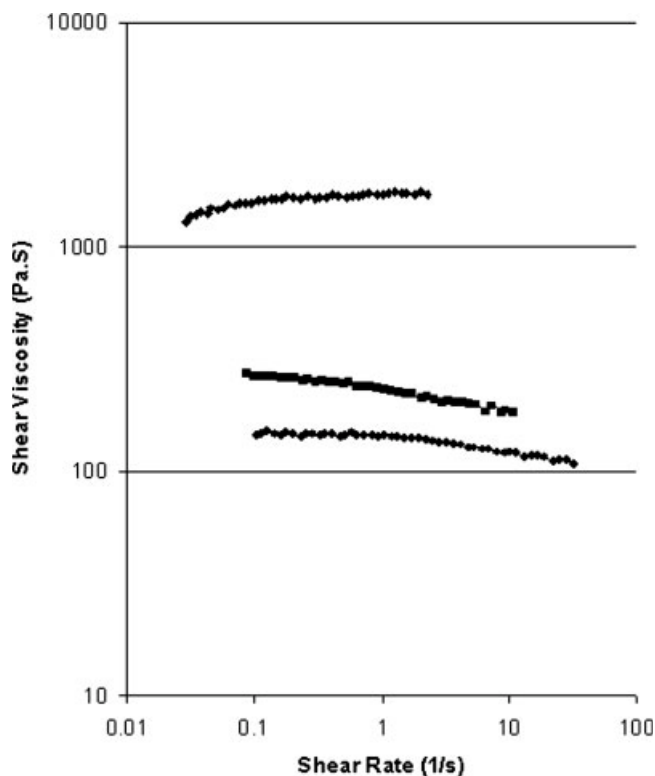


Figure 1 Viscous behavior of virgin polymers at 260°C: \diamond virgin PC; \blacksquare virgin PET; and \bullet virgin PBT.

RESULTS AND DISCUSSION

Rheological properties

Figure 1 shows the variation of shear viscosity with shear rate for virgin polymers at 260°C. Viscosity of PC is much higher than that of both the polyesters. Among the polyesters PET has higher viscosity than PBT.

Rheological behavior of PC-PBT blends with added catalyst

Figures 2–9 show the effect of mixing time and amount of catalyst on the rheology of PC-PBT blends. The blend designated 0 min represent no catalyst and the blend prepared from extruder as outlined earlier. From the results shown in Figure 2, there appears to be a systematic trend in variation of viscosity. As the time of mixing has increased, shear viscosity is reduced.

Figure 3 shows that the viscosity of PC-PBT blend has reduced significantly after 15 min of mixing with no catalyst. By adding 0.1 and 0.2 phr of catalyst, the viscosity is reduced further. The color of blend after 15 min of mixing was found to be tending towards yellow brown shade that may be due to the formation of butylene carbonates. The formation of ethylene carbonate during trans esterification between PC and

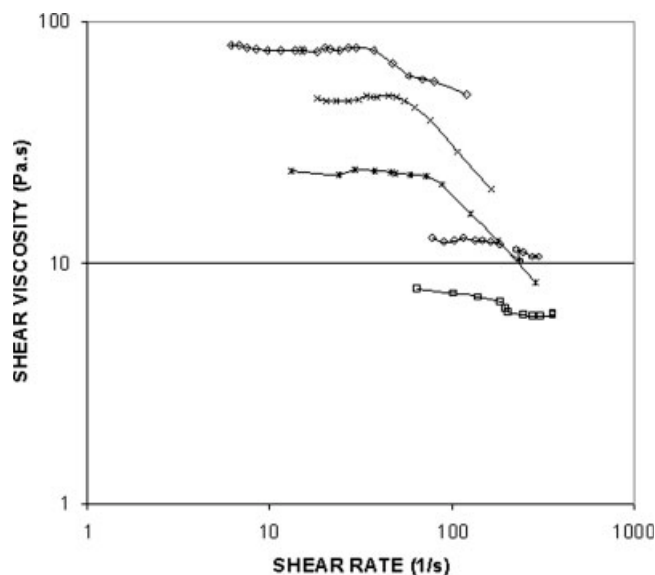


Figure 2 Viscous behavior of pc-pbt blends with added catalyst at 260°C: \diamond PC : PBT 60 : 40 0 min; \square PC : PBT 60 : 40 15 min (0.1 catalyst); \times PC : PBT 60 : 40 2 min (0.1 catalyst); $*$ PC : PBT 60 : 40 4 min (0.1 catalyst); and \circ PC:PBT 60 : 40 8 min (0.1 catalyst).

PET is reported by other researchers.^{21–24} Along similar lines, therefore, butylene carbonate can be formed for PC/PBT blends. Ethylene carbonate is yellow brown in color. The change in color can be due to for-

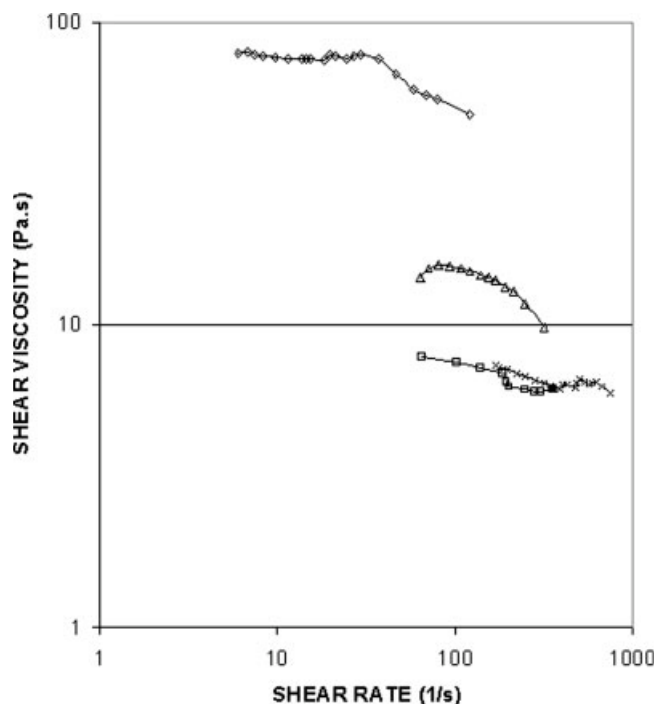


Figure 3 Viscous behavior of PC-PBT blends for 15 min of mixing at 260°C: \diamond PC : PBT 60 : 40 0 min; \square PC : PBT 60 : 40 15 min (0.1 catalyst); \triangle PC : PBT 60 : 40 15 min (no catalyst); and \times PC : PBT 60 : 40 2 min (0.1 catalyst).

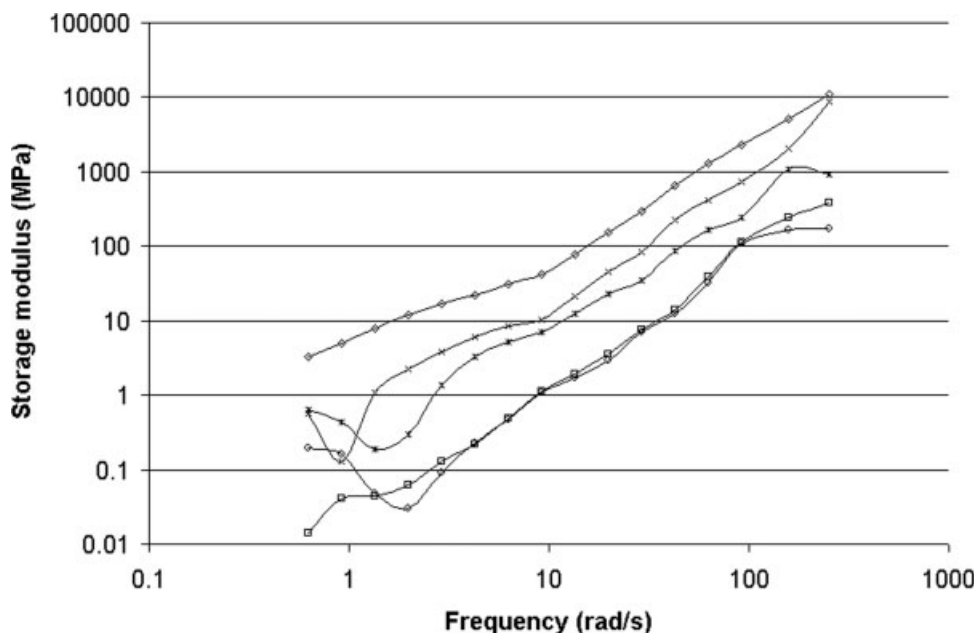


Figure 4 Storage modulus of PC-PBT blends with added catalyst at 260°C: \diamond PC:PBT 60 : 40 0 min; \square PC : PBT 60 : 40 15 min (0.1 catalyst); \times PC : PBT 60 : 40 2 min (0.1 catalyst); * PC : PBT 60 : 40 4 min (0.1 catalyst); and \circ PC : PBT 60 : 40 8 min (0.1 catalyst).

mation of carbonate or also due to thermal degradation. This needs further study. The decrease in viscosity at the end of 15 min of mixing is same whether the catalyst is 0.1 or 0.2 phr. The decrease in viscosity is more as compared to viscosity of blend without cata-

lyst. When catalyst is added, even after 2 min, there is significant decrease in viscosity.

Figures 4 and 5 show variation of storage modulus G' . It is very clear that storage modulus decreases with increasing mixing times. Figures 6 and 7

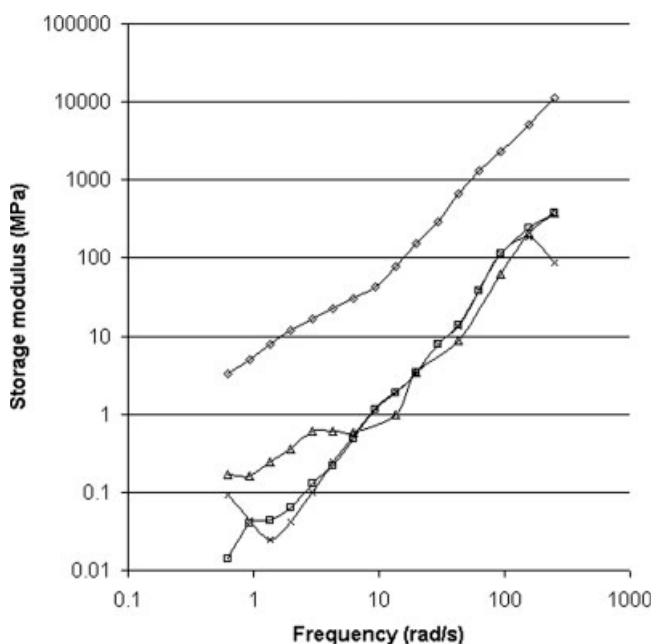


Figure 5 Storage modulus of PC-PBT blends for 15 min of mixing at 260°C: \diamond PC : PBT 60 : 40 0 min; \square PC : PBT 60 : 40 15 min (0.1 catalyst); \triangle PC : PBT 60 : 40 15 min (no catalyst); and \times PC : PBT 60 : 40 15 min (0.2 catalyst).

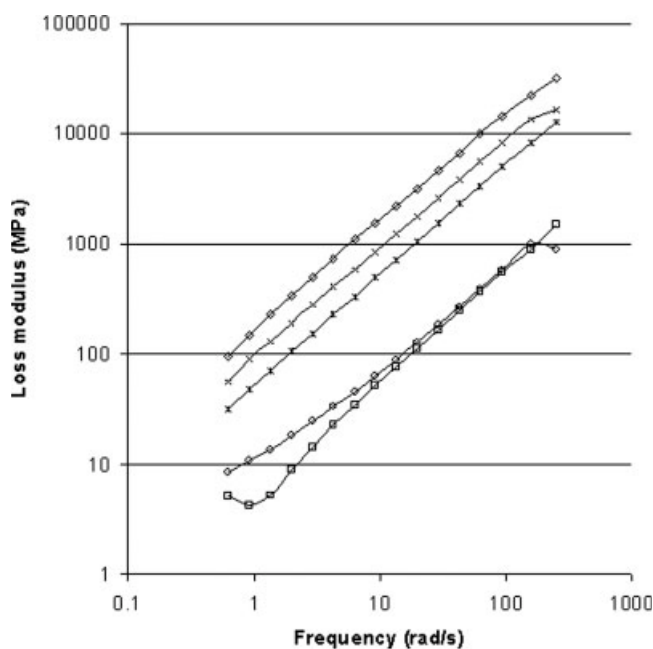


Figure 6 Loss modulus of PC-PBT blends with added catalyst at 260°C: \diamond PC : PBT 60 : 40 0 min; \square PC : PBT 60 : 40 15 min (0.1 catalyst); \times PC : PBT 60 : 40 2 min (0.1 catalyst); * PC : PBT 60 : 40 4 min (0.1 catalyst); and \circ PC : PBT 60 : 40 8 min (0.1 catalyst).

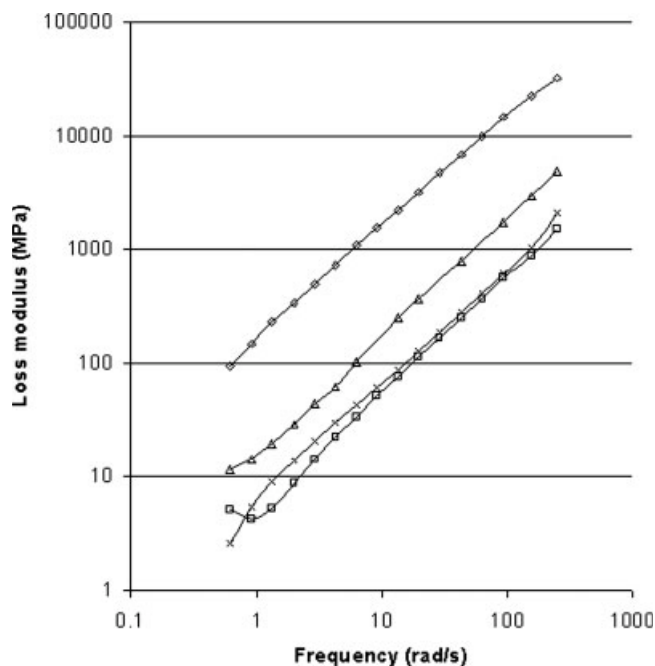


Figure 7 Loss modulus of PC-PBT blends for 15 min of mixing at 260°C: \diamond PC:PBT 60 : 40 0 min; \square PC : PBT 60 : 40 15 min (0.1 catalyst); \triangle PC : PBT 60 : 40 15 min (no catalyst); and \times PC : PBT 60 : 40 15 min (0.2 catalyst).

show variation in loss modulus. The loss modulus also has reduced and the reduction shows systematic variation with mixing time.

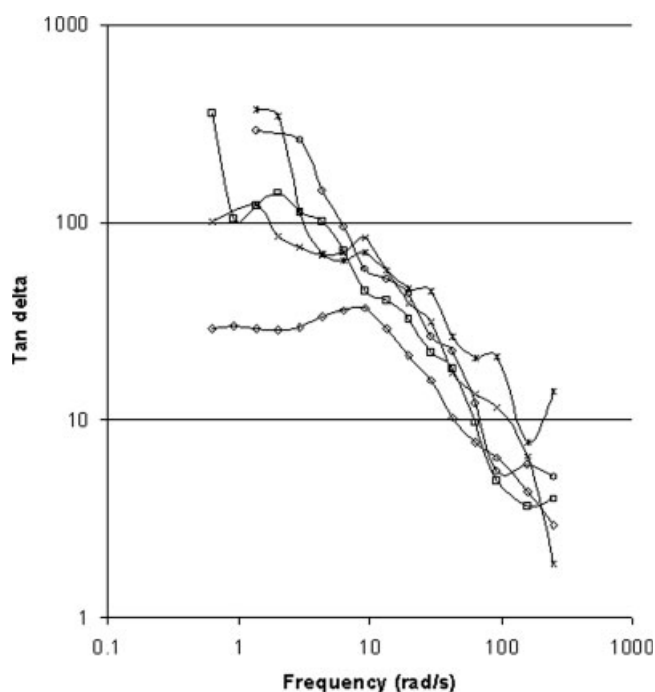


Figure 8 $\tan \delta$ of PC-PBT blends with added catalyst at 260°C: \diamond PC : PBT 60 : 40 0 min; \square PC : PBT 60 : 40 15 min (0.1 catalyst); \times PC : PBT 60 : 40 2 min (0.1 catalyst); * PC : PBT 60 : 40 4 min (0.1 catalyst); and \circ PC : PBT 60 : 40 8 min (0.1 catalyst).

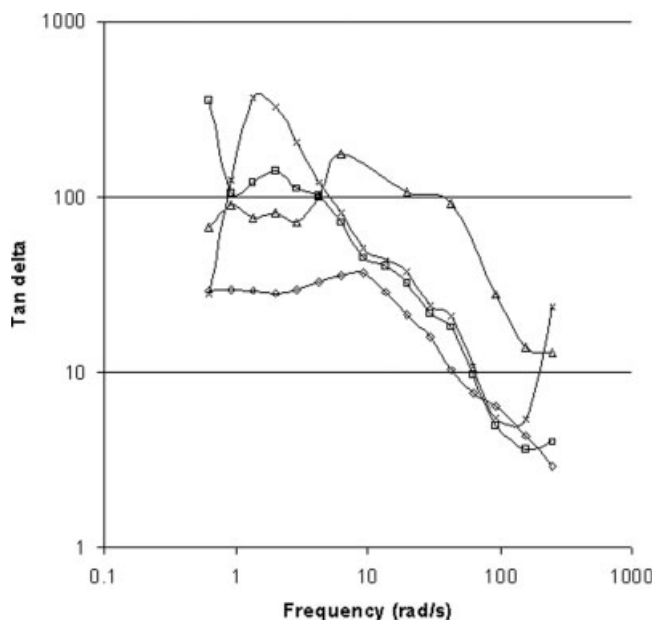


Figure 9 $\tan \delta$ of PC-PBT blends for 15 min of mixing at 260°C: \diamond PC : PBT 60 : 40 0 min; \square PC : PBT 60 : 40 15 min (0.1 catalyst); \triangle PC : PBT 60 : 40 15 min (no catalyst); and \times PC : PBT 60 : 40 15 min (0.2 catalyst).

Figures 8 and 9 show the variation in $\tan \delta$ with frequency. Value of $\tan \delta$ has increased with time of mixing and presence of catalyst. This obviously indicates the reduction in storage modulus is much more than that of loss modulus. The variation in $\tan \delta$ indicates

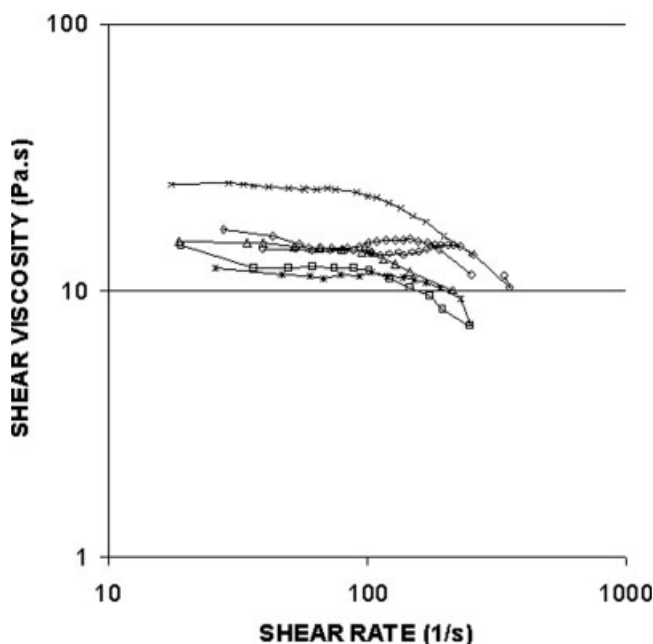


Figure 10 Viscous behavior of PC-PET blends with added catalyst at 260°C: \diamond PC : PET 60 : 40 0 min; \square PC : PET 60 : 40 2 min (0.1 catalyst); \times PC : PET 60 : 40 8 min (0.1 catalyst); * PC : PET 60 : 40 15 min (0.1 catalyst); \circ PC : PET 60 : 40 15 min (0.1 catalyst); and \triangle PC : PET 60 : 40 4 min (no catalyst).

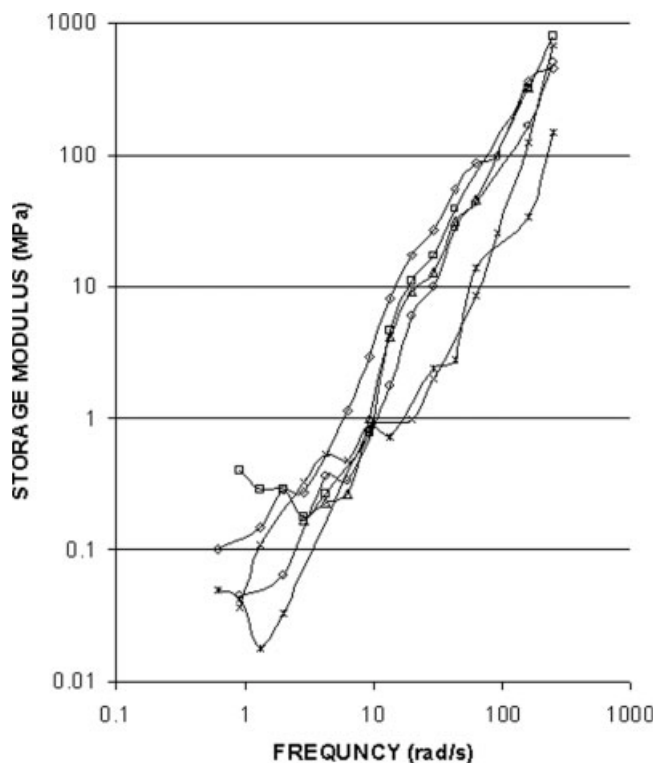


Figure 11 Storage modulus of PC-PET blends with added catalyst at 260°C: \diamond PC : PET 60 : 40 0 min; \square PC : PET 60 : 40 2 min (0.1 catalyst); \times PC : PET 60 : 40 8 min (0.1 catalyst); * PC : PET 60 : 40 15 min (0.1 catalyst); \circ PC : PET 60 : 40 15 min (0.1 catalyst); and \triangle PC : PET 60 : 40 4 min (no catalyst).

that the resulting blends will behave more like a viscous liquid and blend will predominantly lose elastic behavior.

The PC-PBT blends are characterized by transesterification by number of researchers. The comparison between transesterification of PC-PET and PC-PBT systems clearly indicates that transesterification between PC-PET is faster as compared to PC-PBT. It is also reported that transesterification product changes to random copolymer. The steady reduction in viscosity of PC-PBT blends with time clearly indicates that random copolymer that could have been formed has lower viscosity as compared to PC or PBT. Possible elimination of butylene carbonate also suggests that resultant molecular weight of random copolymer could be less. Possible formation of ethylene carbonate or butylene carbonate would result in polymer with lesser molecular weight. Lower molecular weight polymer would have lower viscosity. This phenomenon needs more detailed investigation. The reduction in viscosity being almost same by the end of 15 min by catalyst seems to suggest that equilibrium may be reached within this much time. The reduction of viscosity even after 2 min in presence of catalyst suggests that after the initial rapid transesterification further rates of transesterification slow down. Since transesterification rates for PC-PET blends are reported to be

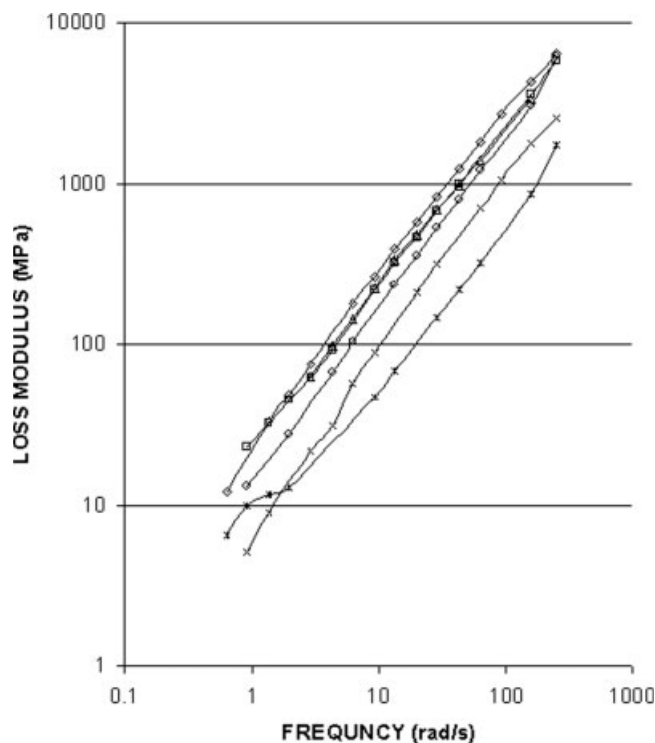


Figure 12 Loss modulus of PC-PET blends with added catalyst at 260°C: \diamond PC : PET 60 : 40 0 min; \square PC : PET 60 : 40 2 min (0.1 catalyst); \times PC : PET 60 : 40 8 min (0.1 catalyst); * PC : PET 60 : 40 15 min (0.1 catalyst); \circ PC : PET 60 : 40 15 min (0.1 catalyst); and \triangle PC : PET 60 : 40 4 min (no catalyst).

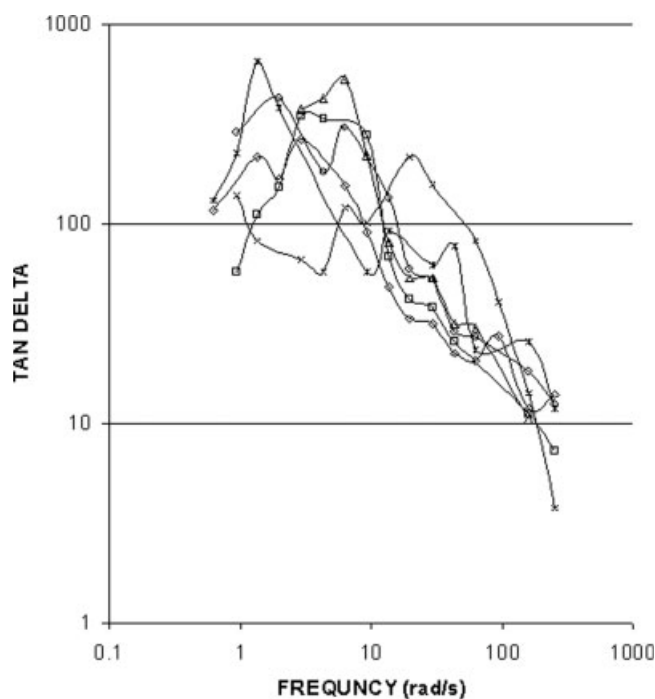


Figure 13 $\tan \delta$ of PC-PET blends with added catalyst at 260°C: \diamond PC : PET 60 : 40 0 min; \square PC : PET 60 : 40 2 min (0.1 catalyst); \times PC : PET 60 : 40 8 min (0.1 catalyst); * PC : PET 60 : 40 15 min (0.1 catalyst); \circ PC : PET 60 : 40 15 min (0.1 catalyst); and \triangle PC : PET 60 : 40 15 min (no catalyst).

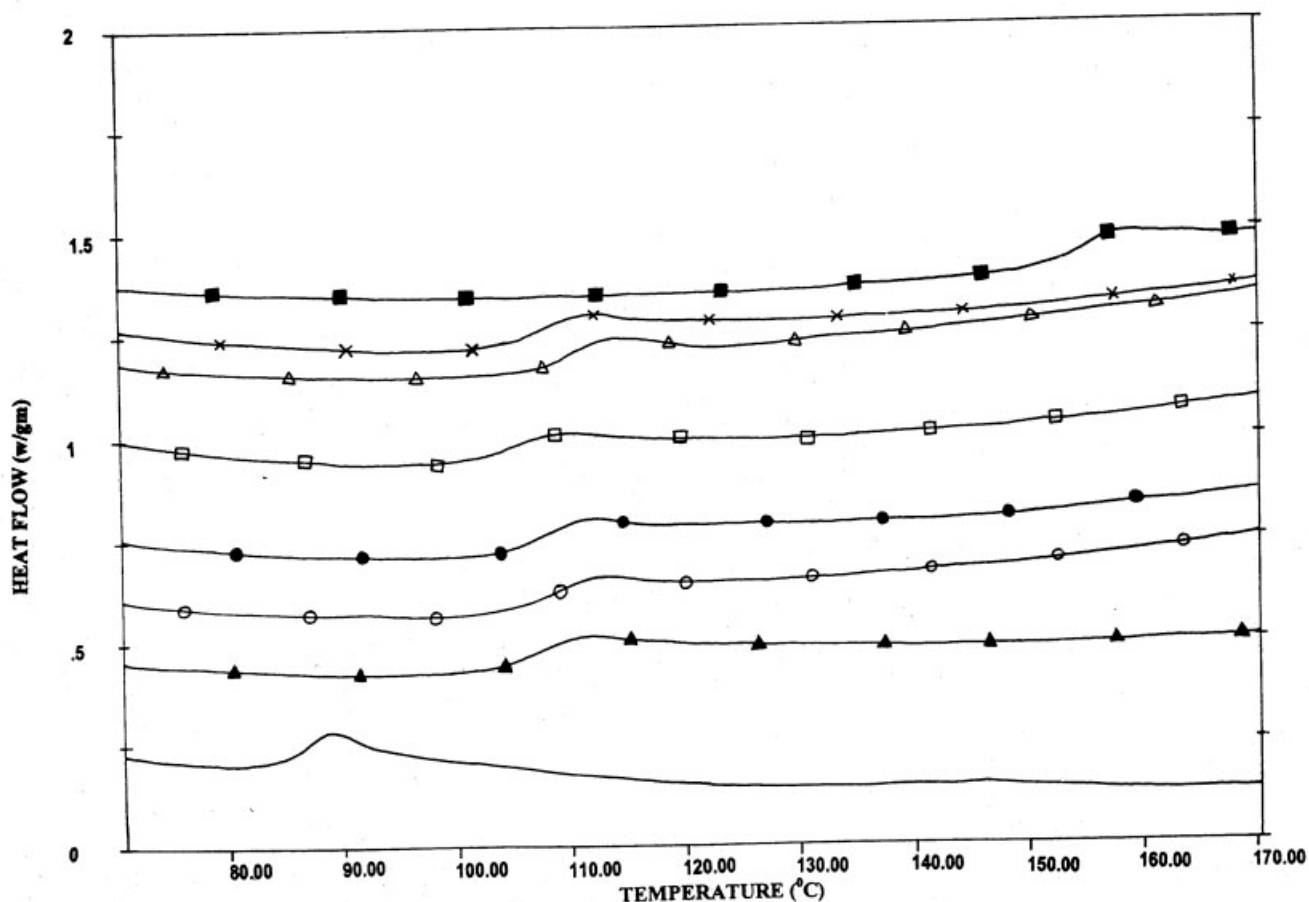


Figure 14 DSC heating thermograms of PC/PET blends with added catalyst: ■ virgin PC; × PC : PET 60 : 40 15 min (0.1 catalyst); △ PC : PET 60 : 40 8 min (0.1 catalyst); □ PC : PET 60 : 40 4 min (0.1 catalyst); ● PC : PET 60 : 40 2 min (0.1 catalyst); ○ PC : PET 60 : 40 15 min (no catalyst); ▲ PC : PET 60 : 40 0 min (No catalyst); and - virgin PET.

higher than that of PC-PBT blends the rheological behavior for it can be different that is shown in Figures 10–13.

Rheological behavior of PC-PET blends with added catalyst

Viscosity of the blend at 0, 2, 4, and 15 min of mixing appear to be comparable. It appears that viscosity of blends is significantly lower than that of PET (and obviously PC). Since the viscosity of the blends is less than that of PC or PET transesterification must have taken place. Addition of catalyst seems to have little effect on viscosity.

Similarly storage modulus (G') and loss modulus (G'') values for the blend with or without catalyst (0 min) appear to be comparable, although these are lower than that of PC or PET.

The random copolymers are amorphous in nature. Therefore, crystallinity of the blends would be less than that for PET or PBT. The studies on DSC are presented next.

Differential scanning calorimeter

Figure 14 shows the DSC scans for heating cycle of PC:PBT blends with added catalyst. It is observed that as the mixing time increased the value of melting peak (T_m) and heat of fusion (ΔH_m) values decreased. No clear T_g 's could be recorded for the blends that were mixed for 0, 2, and 4 min. The composition with 8 min of mixing, two T_g 's are observed. After 15 min of mixing, the catalyzed blends show only one single T_g about 90°C. The T_g for PC phase seems to decrease steadily as time of mixing has increased. The T_g about 90°C after 15 min of mixing is also been observed by Wilkinson et al.³⁰ If one estimates T_g for random copolymer of 60% PC and 40% PBT the value is about 86°C by applying Fox equation. The DSC data are tabulated in Table II.

Figure 15 shows the DSC scans for heating cycle of PC:PET blends. All the blends show single glass transition temperature (T_g) about 106°C. This value is much lower than that for PC. The blend designated as 0 min (which is extruded blend with no catalyst) also shows T_g about 106°C, which indicates that the resid-

TABLE II
Thermal Properties of All the Blends with Added Catalyst

Compositions	T_g polyester ($^{\circ}\text{C}$)	T_g PC ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)
<i>PC-PET blends</i>				
0 min, no catalyst (Batch 1)	106			
2 min, 0.1 catalyst (Batch 2)	107.3			
4 min, 0.1 catalyst (Batch 3)	104.4			
15 min, 0.1 catalyst (Batch 4)	106.6			
15 min, no catalyst (Batch 5)	106.8			
<i>PC-PBT blends</i>				
0 min, no catalyst (Batch 6)	–	–	228.6	16.81
2 min, 0.1 catalyst (Batch 7)	–	–	226.3	25.44
4 min, 0.1 catalyst (Batch 8)	–	–	216.1	18.13
8 min, 0.1 catalyst (Batch 9)	92.5	131.1	–	–
15 min, 0.1 catalyst (Batch 10)	91.0	–	–	–
15 min, 0.2 catalyst (Batch 11)	89.0	–	–	–
15 min, no catalyst (Batch 12)	–	–	215.2	17.96

ual catalyst that is present in commercial PET sample is sufficient for transesterification. None of the compositions show the presence of melting peak (T_m). These indicates the formation of random copolymer in PC-PET blends that also supports rheological observations.

CONCLUSIONS

Rheology of PC-PBT blends seems to show systematic variation with time of mixing. Similarly, DSC data also show the systematic variation. However, for PC-PET blends, the processing time in an extruder and

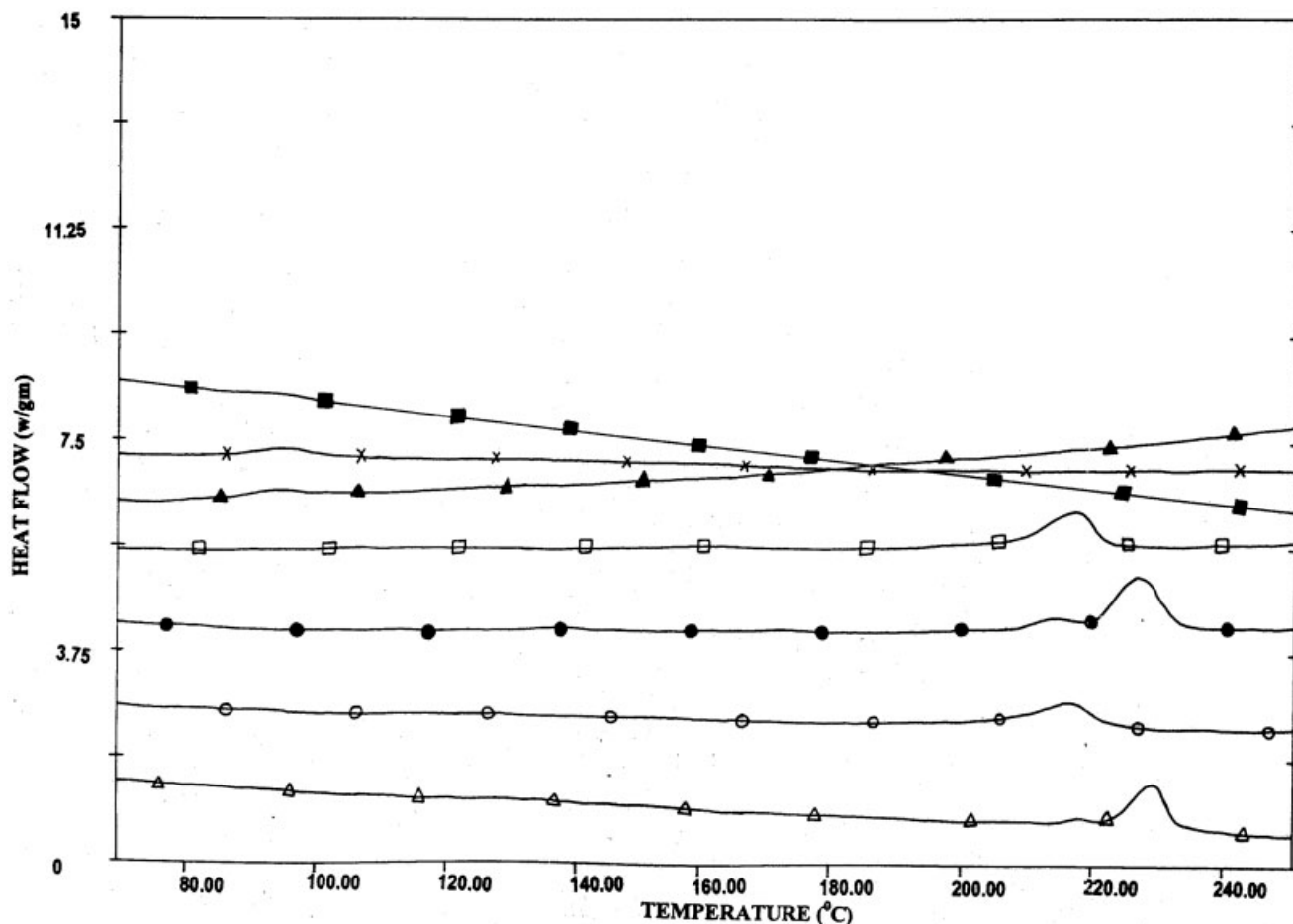


Figure 15 DSC heating thermograms of PC/PBT blends with added catalyst: ■ PC : PBT 60 : 40 15 min (0.2 catalyst); × PC : PBT 60 : 40 15 min (0.1 catalyst); ▲ PC : PET 60 : 40 8 min (0.1 catalyst); △ PC : PET 60 : 40 4 min (0.1 catalyst); ● PC : PET 60 : 40 2 min (0.1 catalyst); ○ PC : PET 60 : 40 15 min (no catalyst); and △ PC : PET 60 : 40 0 min (no catalyst).

residual catalyst present in the commercial sample cause sufficient degree of transesterification. The formation of random copolymer show significantly lower viscosity than PC, PET, and PBT. The elastic properties of random copolyester also seem to be reduced. Random copolymers also are amorphous in nature as indicated by reduction in ΔH_m values. The T_g of these copolymers seems to agree with equilibrium composition and with Fox equation.

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