# Shear rheology and thermal properties of linear and branched poly(ethylene terephthalate) blends

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## Abstract

Linear poly(ethylene terephthalate) (LPET) was blended with branched poly(ethylene terephthalate) (BPET) by varying the branching comonomer and blend proportion of BPET. The crystallinity and melting temperatures of LPET in blends with BPET was measured using differential scanning calorimetry (DSC). Thermal analysis revealed that the crystallinity and crystallisation/melting temperatures of LPET–BPET blends were increased compared with LPET. The rheological measurements of the blends were conducted using a controlled stress rheometer, with dynamic oscillatory shear, as well as steady shear measurements. The acceleration of the LPET crystallisation was dependent on the blend proportion and on the branching comonomer. The rheological measurements indicated a 50% increase of melt viscosity of LPET when blended with 30 mass% of BPET. This was attributed to increasing chain entanglements with the proportion of branching comonomer of the BPETs. Also, blends of LPET with BPET of different branching comonomer were investigated, and the rheology was found to be highly sensitive to composition. Dynamic rheological measurements of the blends were made, and compared with the data for LPET, to evaluate the effect of BPET on the viscoelasticity. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Branched poly(ethylene terephthalate); Blend proportion; Crystallisation

## 1. Introduction

Polymer modification through blending has received considerable interest during the last several decades. A significant number of commercial blends have become available and continuous efforts are expected to further create more desirable morphologies for thermal, rheological and mechanical properties. The rheology of blends is important because the mechanical properties of blends are greatly dependent on deformation history [1].

Polymer blends have recently become attractive both for industrial application and theoretical interest. They have been found to be useful for the preparation of more convenient and available products than by developing new polymers through monomer synthesis and polymerisation [2]. Poly(ethylene terephthalate) (PET) is one of the engineering plastics that has been studied as a component of many polymer blends. It is a versatile polymer used in synthetic fibres, films, blow-moulded containers and injection-moulded engineering components. Blending it with a variety of crystalline and amorphous polymers [3] can modify the properties of melt-processed articles of PET. One of the primary factors affecting the mechanical properties of

semicrystalline PET is related to its crystalline and amorphous regions in the morphological structures [4].

Another approach that has received little attention is to blend linear poly(ethylene terephthalate) (LPET) with branched poly(ethylene terephthalate) (BPET). Blending LPET with the BPET is expected to be useful for recycling PET, as recycled PET is partially degraded. Degradation occurs as a result of its prior processing, its exposure to the environment during use, and its subsequent separation and granulation. The blends are expected to show a higher melt viscosity with a pronounced yield value, or a high viscosity at low shear rates/frequencies because of the properties of BPET and because of their similar chemical structures, they are expected to provide a uniform morphology.

BPET has been shown to have significant shear thinning behaviour with a high zero shear viscosity [5]. This was caused by a relatively small number of branches. LPET however shows mild shear thinning behaviour. Therefore, it was expected that BPET would substantially change the rheology of LPET in a blend.

In this research, several LPET–BPET blends were prepared by varying the branching comonomer and blend proportions of BPET. It is relevant, that the melt viscosity behaviour as well the crystallisation behaviour of LPET–BPET blends will be influenced by the amount of branching

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Table 1
Codes for BPET–LPET blends prepared

| Composition (mass%) | Code | $T_c$ (°C) | $T_m$ (°C) |
|---|---|---|---|
| 20 : 80 | PETg 20 | 206.9 | 251.3 |
| 30 : 70 | PETg 30 | 213.1 | 252.2 |
| 40 : 60 | PETg 40 | 209.4 | 251.5 |
| 20 : 80 | PETp 20 | 219.3 | 252.8 |
| 100 : 0 | Bgd | 205.4 | 247.1 |
| 100 : 0 | Bpd | 219.3 | 251.8 |
| 0 : 100 | LPET | 180.8 | 246.1 |

comonomer and the type of functional comonomer in the BPET. Several dynamic and steady shear rheological properties such as shear stress, apparent viscosity, complex viscosity, storage modulus, and loss modulus were investigated.

## 2. Experimental

### 2.1. Materials and blending method

The BPETs were synthesised using the method of polymerisation described in a previous paper [6]. All BPET samples were characterised by measurement of the limiting viscosity number. The amount of branching was taken as the mole percent of branching comonomer in the PET, so polymers with pentaerythritol (functionality = 4) will have more branches than polymers with glycerol (functionality = 3) even though they are nominally shown as having the same amount of branch points. The branches in BPET with pentaerythritol will have two branches emanating from the one carbon; they could alternatively be described as an intersection of two chains. The LPET used for blends was

obtained from a soft drink bottle grade. The LPET was blended with BPET with different branching comonomer and with different blend proportions. The blends were prepared by mixing solutions of polymers previously dissolved in phenol–tetrachloroethane solvent (1 : 1 by mass). The solution mixing was then followed by precipitation with methanol and formation of a finely divided form of the blend. After blending, the samples were dried at 140°C for 48 h in a vacuum oven. The blend with BPET having pentaerythritol as comonomer for branching was designated PETp and the ones having glycerol as comonomer for branching as PETg. The codes for each sample examined in this article are listed in Table 1.

### 2.2. Differential scanning calorimetry

The blends (3 ± 0.5 mg) were analysed using a Perkin-Elmer DSC7 for crystallisation and melting studies. The samples were dried at 80°C for 24 h before DSC measurements. The crystallisation and melting temperatures were determined at cooling and heating rates of 5°C min$^{-1}$ under a nitrogen atmosphere. The samples were first heated to 280°C for 3 min, then cooled at 5°C min$^{-1}$ to 40°C for 2 min and then heated at 5°C min$^{-1}$ again to 280°C for 1 min. Both crystallisation and melting parameters were obtained from the cooling and heating thermograms.

### 2.3. Melt rheology

Dynamic and steady shear rheological measurements were carried out on a Rheometrics SR 200 dynamic stress rheometer. This operates at a controlled stress where the stress is applied to the material and its resulting strain rate is measured. The instrument required only a small volume of material so rapid temperature equilibrium was achieved. The tests were performed at temperatures ranging from
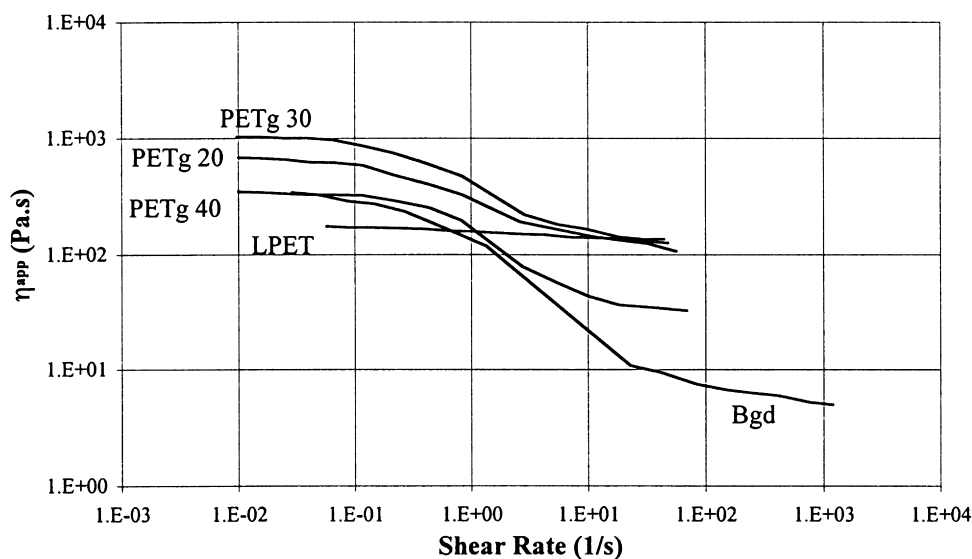


Fig. 1. Steady shear viscosity vs. shear rate at 260°C of LPET–PETg blends with the same branching comonomer and with different blend proportions and Bgd.
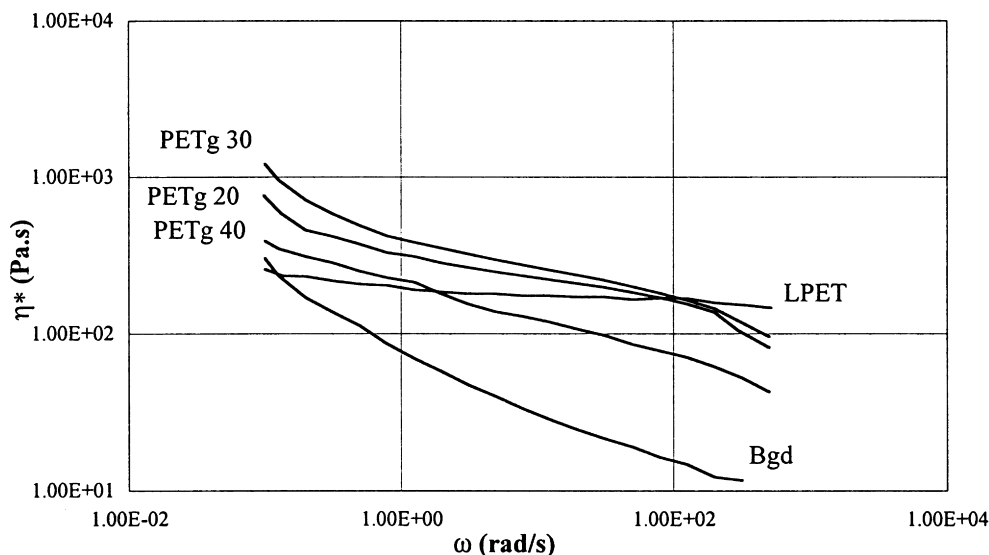
Fig. 2. Frequency dependence of $\eta^*$ at 260°C of LPET–PETg blends with the same branching comonomer and with different blend proportions and Bgd.

260°C to 270°C for a period of about 5–10 min; the samples were found to be thermally stable under these conditions by testing a sample at constant stress for 30 min at 270°C. Before each test, the blends were dried under vacuum at 80°C for 24 h, and each blend sample was compression moulded under a nitrogen atmosphere to prevent polymer degradation. The steady shear viscosity and the dynamic viscosity measurements were determined using a 25 mm diameter parallel plate geometry with a constant gap spacing. For dynamic tests, the strain ($\gamma$) values were chosen in order to perform the experiments in the linear viscoelastic region (LVR) i.e., the limiting strain under which the rheological parameters ($G'$, $G''$, $\eta^*$, etc.) remained constant. For this purpose, a preliminary study was made at 270°C and the LVR was determined for each blend. The strain amplitude was varied from 0.2% to 15%, to keep the tests within this region over a frequency range of $0.1–500 \text{ rad s}^{-1}$.

## 3. Results and discussion

### 3.1. Rheological data

The steady shear apparent viscosity ($\eta_{app}$) obtained at a temperature 260°C for LPET–PETg blends with the same branching comonomer and different blend proportions of BPET is presented as a function of shear rate (1/s) in Fig. 1. The differences in melt viscosity of LPET–BPET blends could be explained by their type of functional comonomer and blend composition. It is seen that the steady shear viscosity at low shear rates is much higher for PETg blends than for LPET. This occurs even when the molar mass of BPET was relatively low [5].

As seen from Fig. 1, the PETg 30 blend had a higher apparent viscosity than the LPET. Further addition of

BPET up to 40 mass% produced less of a decrease in viscosity than the PETg 20 blend. Melt strength can be associated with zero shear viscosity and has shown a proportional relationship with the entanglement density of the polymers [7]. The viscosity increases as the entanglement density increases. When melt viscosity becomes constant at very low shear rates it is called the zero-shear viscosity. The zero shear viscosity is increased with an increase in blend proportions.

As a result of a greater degree of chain branching, LPET–BPET blends were expected to exhibit a greater entanglement density than LPET. In the near zero shear viscosity (low shear stress) region, which is of special interest for polymer characterisation and where the rheological response depends on the size of the macromolecular random coil and specific interactions among macromolecules [8]. The viscosity was proportional to the amount of BPET for all blends investigated. The LPET–BPET blends also exhibited significant shear thinning, so that their melt viscosity decreased to become lower than linear PET at high shear rates [9]. In the near zero shear viscosity region the steady shear viscosity of blends is higher than that of linear PET, indicating larger levels of interactions in the blends than for the pure LPET. Another feature shown by these blends is that a rapid rise of the flow curve with decreasing shear rates was observed.

The frequency ($\omega$) dependence of the dynamic complex viscosity ($\eta^*$) obtained at 260°C for PETg blends and LPET, with the same branching comonomer and different amounts of BPET is presented in Fig. 2. In the dynamic melt rheology, the blends with the same branching comonomer showed a similar decrease in viscosity as the shear thinning that was observed (similar slopes) in steady flow, with an increase in blend proportion. The increase in dynamic melt viscosity with increasing blend proportion was caused by the higher viscosity of the branched polymers. The increase
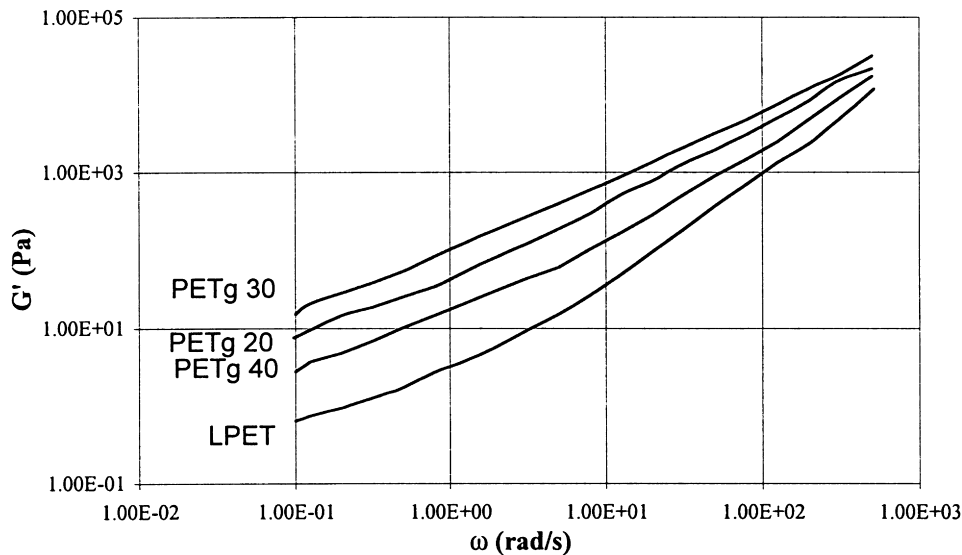
Fig. 3. Storage shear modulus vs. frequency at 260°C for LPET–PETg blends with the same branching comonomer and with different blend proportions.

in non-Newtonian character of LPET–BPET blends is also considered to be caused by the entanglements of the branched molecules. With the exception of PETg 40, the curves for PETg 30 and PETg 20 approached each other at high frequencies.

Fig. 3 shows the storage modulus ($G'$) as a function of frequency for LPET and PETg blends with same branching comonomer and different blended proportions obtained at 260°C. As $G'$ is associated with an index of melt elasticity [10], the results shown in Fig. 3 imply that the elasticity is enhanced with the addition of branching comonomer (amount in the blend). The PETg blends approach a plateau (PETg 30) at high frequency as the branches become disentangled, the molecules will be able to move more readily. This frequency increases with an increase in the amount of branching comonomer content. The differences in elastic behaviour between the two poly(ethylene terephthalates) (LPET and BPET) is thought to be because of the presence of long chain branched macromolecules in the BPET melt.

As seen from Fig. 4, $\eta^*$ is presented as a function of frequency at 260°C for LPET–BPET blends with different branching comonomer and the same blend proportion. A 20 mass% proportion of BPET imparts a large change on the rheological properties on LPET. The dynamic measurements showed distinct trends where the viscosity decreased markedly with frequency, particularly for PETp. The blend with pentaerythritol (PETp) as comonomer for branching showed a higher viscosity than the blend with glycerol (PETg) as comonomer for branching, owing to the functionality of the branching comonomer and the amount in the blend. When BPET was prepared with pentaerythritol as a branching comonomer, there was a rapid increase in $M_w$
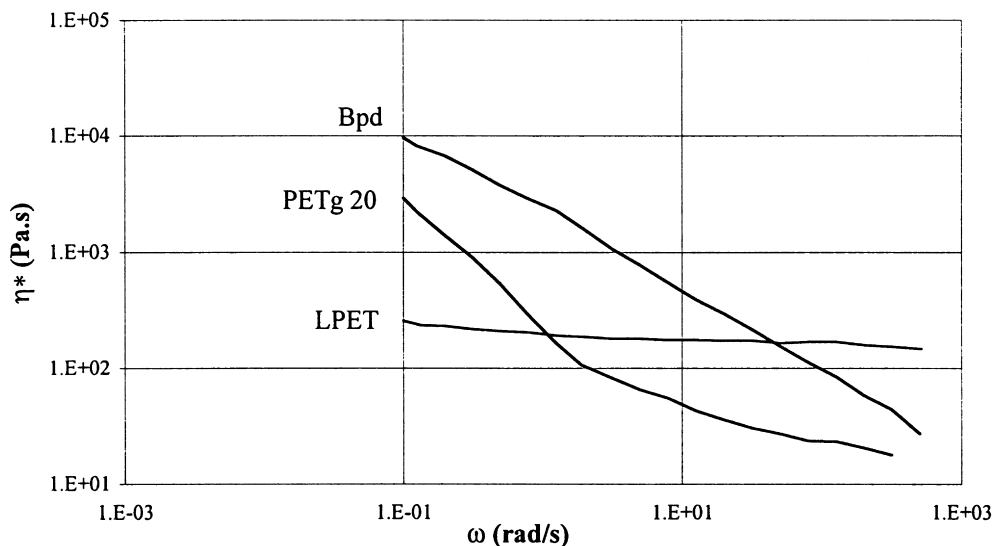


Fig. 4. Frequency dependence of $\eta^*$ at 260°C of LPET–BPET blends with different branching comonomers and with the same blend proportion.
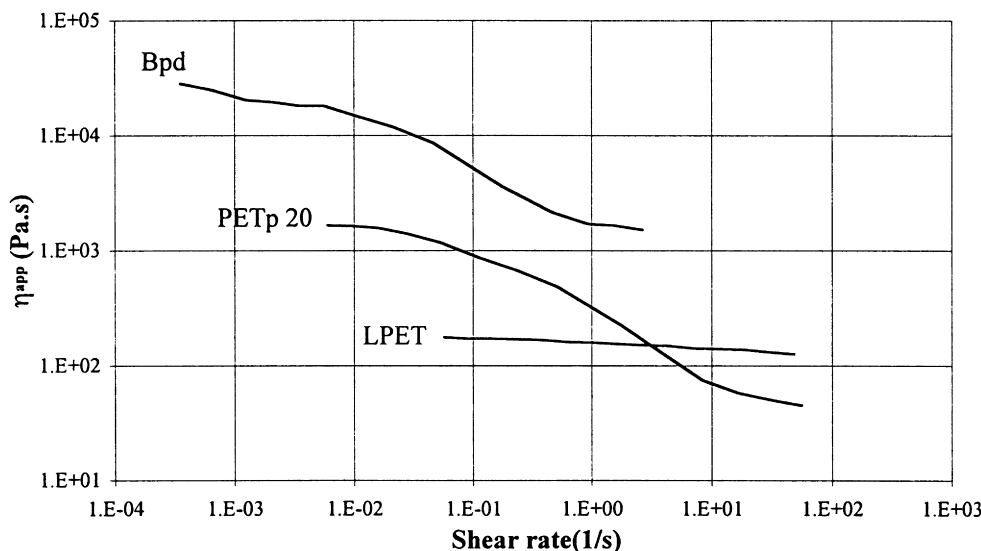
Fig. 5. Steady shear viscosity vs. shear rate at 260°C of LPET–BPET blends with different branching comonomers and with the same blend proportion.

owing to increased functionality compared with glycerol [5].

Another factor, which contributed to the difference in viscosity between the two blends, is the amount of branching comonomer, i.e., PETp and PETg had 2% and 5% comonomer, respectively. The viscosity increases as the amount of branching is increased. The enhancement of complex viscosity and the increase in the non-Newtonian character of blends is probably caused by the decreased mobility of branched molecules. This effect counteracts the decreased regularity of the structure provided by the branched molecules.

Fig. 5 illustrates the shear rate dependency of steady shear viscosity for LPET–BPET blends with different branching comonomer and the same blend proportion. The PETg as well as PETp exhibited significant shear thinning such that their melt viscosity decreased to become lower than LPET at high shear rates. When comparing the PETg blend with the PETp blend, both with same proportion of comonomer, it was seen that PETp exhibited a much higher viscosity than PETg because of increased functionality. Increasing functionality gives increased viscosity, with increasing zero shear viscosity, as expected. The molecules become more bulky rather than just longer with increase in branching composition (functionality). The dependence of zero shear viscosity on $M_w$ can be attributed to the entanglement density provided by the branching comonomer. In steady flow, an increase in shear rate can disentangle the chains, thus causing a lower viscosity [7]. The greater shear thinning of the LPET–BPET blends provides a lower viscosity at higher shear rates than for LPET. Thus addition of BPET to LPET will facilitate processing by extrusion or injection
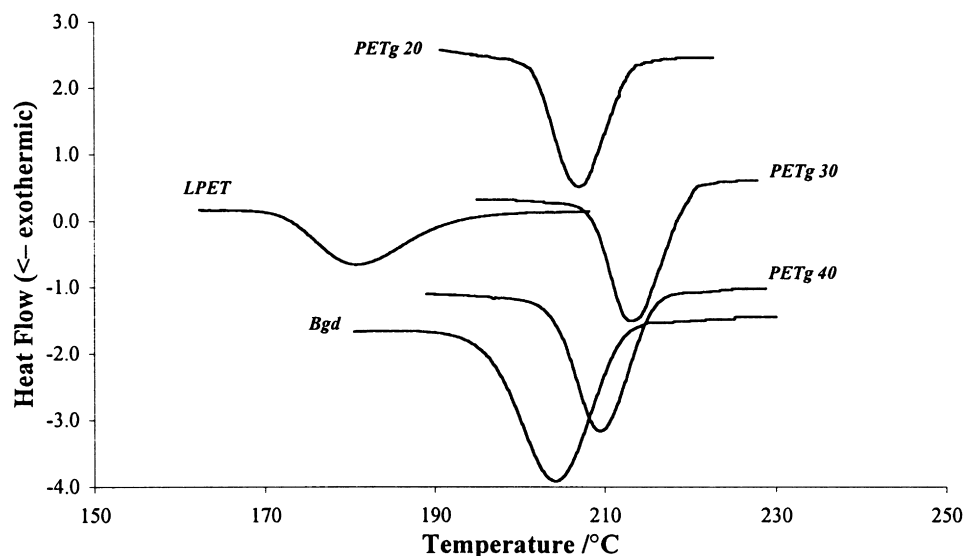


Fig. 6. DSC crystallisation scans of LPET–BETg blends with the same branching comonomer and with different blend proportions, Bgd and LPET.
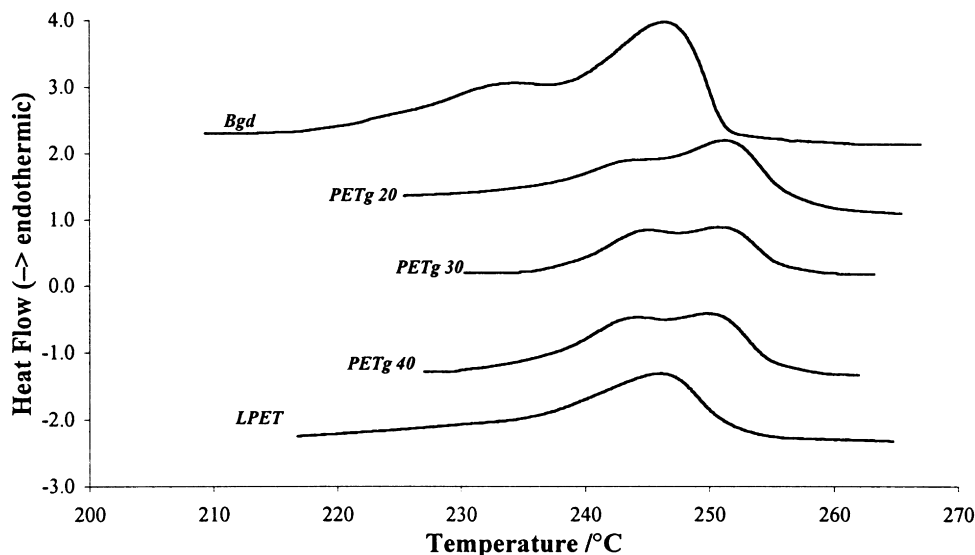
Fig. 7. DSC melting scans of LPET–BPETg blends with the same branching comonomer and with different blend proportions, BPET and LPET.

moulding. The higher zero shear rate viscosity, or melt strength, of the blends will provide better performance in blow moulding, vacuum forming or even film production. The addition of BPET to LPET will therefore overcome one of its serious deficiencies, low melt strength.

This is particularly true of recycled PET where degradation will have further reduced melt strength. BPET can be used as a processing enhancement for recycled PET. Blending BPET with recycled PET should prove more cost effective and simpler than the various chain lengths increasing reactions, which must be performed on the recycled PET.

### 3.2. DSC analysis

It is known that the crystallisation behaviour of a polymer

becomes modified in a blend because of the presence of the other component. All LPET–BPET blends showed only one distinctive crystallisation exotherm in the crystallisation scan, whereas in the melting scans, two endothermic peaks were observed. The curves of the DSC crystallisation and melting scans of LPET–PETg with the same branching comonomer and different blended proportions are illustrated in Figs. 6 and 7, respectively.

From the thermograms, the LPET exhibited a rather broad temperature range for crystallisation and melting respectively, starting at a lower temperature than either blend. The LPET–PETg blends showed a substantial increase in the crystallisation and melting temperatures. The exotherms were narrower and sharper, and the temperature for crystallisation of the blends was higher than for the LPET. For melting, the endotherms exhibited a broader
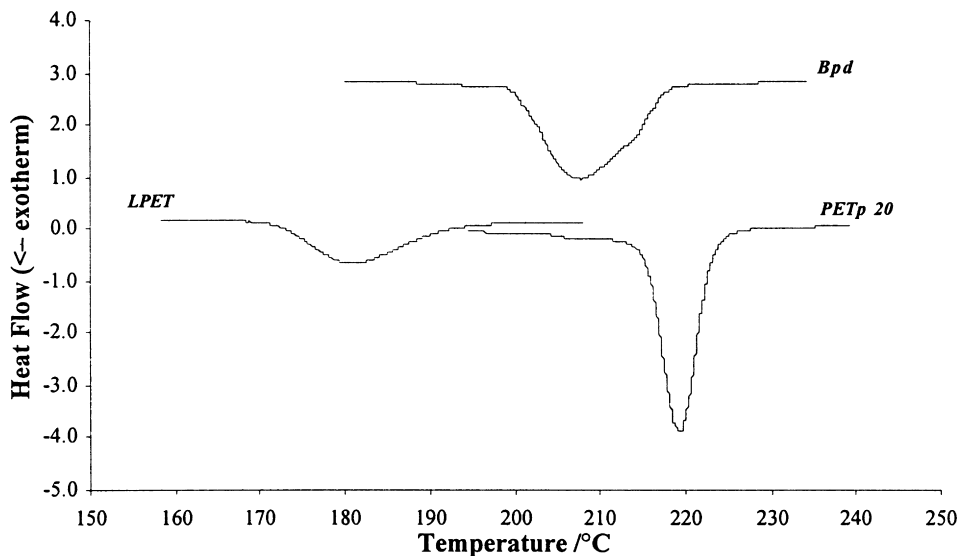


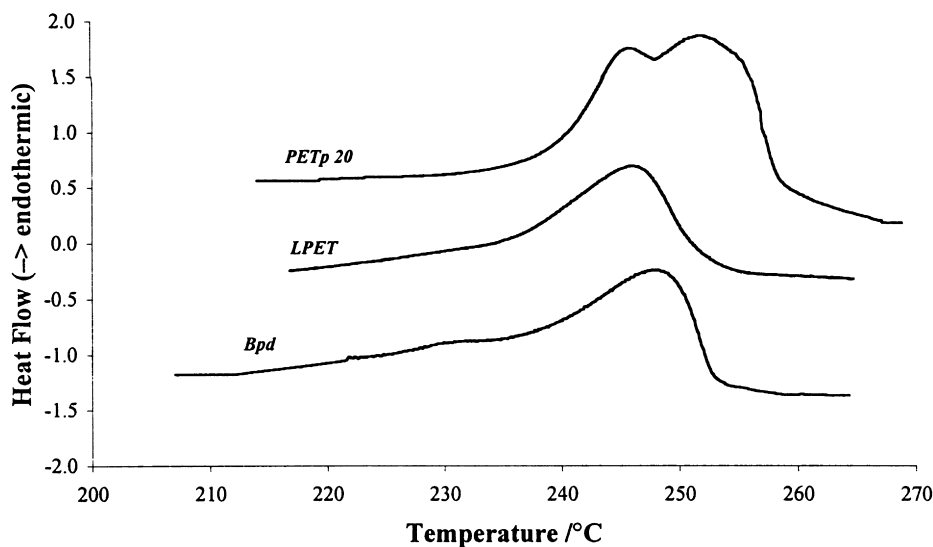Fig. 8. DSC crystallisation scans for LPET, BPET (Bpd) and their blend.

Fig. 9. DSC melting scans for LPET, BPET (Bpd) and their blend.

range and two peaks were observed. The results seem to reveal that the blends with lower BPET content (≤30 mass%) accelerate both crystallisation and melting kinetics of LPET, whereas the blends with higher amounts (=40%) showed an inverse effect. The enhancement of crystallisation and melting temperatures was probably caused by the increased local mobility of the branched molecules. Also the degree of crystallinity of the LPET–PETg blends with 20–40 mass% had increased significantly compared with LPET crystallinity.

The crystallisation and melting were significantly changed for the LPET–BPET blends with different branching comonomer and the same blend proportion as seen in Figs. 8 and 9. The LPET–BPET blend having pentaerythritol as comonomer for branching (PETp) exhibited the higher crystallinity as well as higher crystallisation and melting temperatures than those of the blend having glycerol as comonomer for branching (PETg). This is because of an increase in mobility brought about by the increased branching and the localisation of the branches at the tetrafunctional site. The melting endotherm of PETp is very sharp and narrow. The temperature range for melting and crystallisation of PETp was compared with the PETg (20 mass%). Variation of the proportion of branching in the LPET–PETg blends revealed that the PETg at 30 mass% in the blend exhibited the highest crystallisation and melting temperatures, whereas the LPET–PETg blend with 20 mass% showed the highest crystallinity among all PETg blends.

The DSC crystallisation, melting and crystallinity results are surprising, considering that the blended BPET will decrease the congruity of the LPET. We attribute these changes to an increase in local mobility of the PET caused by having some branching. PET is generally slow to crystallise and so a more mobile structure will be favourable. When the BPET content exceeded 40 mass% the effect reversed and irregularity predominated. This enhancement of crystallisation is a further gain to be made by using BPET as an additive in recycled PET.

## 4. Conclusion

Blends of LPET–BPET show significant changes in rheology and crystallisation–melting compared with the pure LPET and BPET. The steady and dynamic shear rheology of LPET–PET polymer blends is dependent on the molecular structure of the BPET. A relatively small proportion of BPET in LPET imparts a large change on the rheological properties of LPET. LPET is almost Newtonian in behaviour. Non-Newtonian behaviour with increased low shear viscosity and increased shear thinning at higher shear rates, in both steady shear and dynamic shear, is apparent for LPET–BPET blends. As the amount of BPET in a blend was increased from 20 to 40 mass%, an increase in the melt viscosity was observed for the PETg blends. The blends containing up 30 mass% of BPET exhibited the largest increase in shear thinning. The LPET–BPET blends with different branching comonomer and the same proportions in the blend, showed a much higher melt viscosity particularly for PETp blends.

DSC analysis showed that the crystallisation and melting temperatures as well as the degree of crystallinity for both cooling, exothermic, and heating, endothermic, scans respectively of LPET were enhanced substantially by blending with BPET. Blending LPET with BPET promoted the overall crystallinity of the LPET. Blending with BPET not only promoted the crystallinity of the LPET–BPET blends, but what is more important for potential applications is that it increased their melt viscosity.

## References

[1] Kim BK. J App Polym Sci 1990;40(11):1805.
[2] Song W, Ou C, Lin C. J App Polym Sci 1996;60(10):1505.
[3] Nadkarin V, Shingankuli L, Jog J. J App Polym Sci 1992;46(11):339.
[4] Fann D, Huang SK, Lee J. J App Polym Sci 1996;61(8):1375.
[5] Rosu RF, Shanks RA, Bhattacharya SN. J Polym Sci B Polym Phys, submitted.
[6] Rosu RF, Shanks RA, Bhattacharya SN. Polym International 1997;42(3):267.
[7] Khanna YP. Poly Eng Sci 1991;31:440.
[8] Micic P, Bhattacharya SN, Field G. International Polym Proc 1996;XI:14.
[9] Mishra SP, Deopura B. Rheolog Acta 1984;23:189.
[10] Utracki LA. Polymer alloys and blends – thermodynamics and rheology. New York: Hanser Pub, 1990:214.