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Phase behaviour, mechanical properties and thermal stability of thermosetting polymer blends of unsaturated polyester resin and poly(ethylene oxide)

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The results of dynamic mechanical analysis reveal that crosslinked polyester resin (PER)/poly(ethylene oxide) (PEO) blends show a composition dependent glass transition temperature, T_g, which suggests that the blends studied are homogeneous in the amorphous state. The initial dynamic storage modulus, E', decreases with increasing PEO content up to 30 wt % in the blends, whereas E for both the 60/40 and 40/60 PER/PEO blends is close to that for the 80/20 PER/PEO blend and much larger than that for the 70/30 PER/PEO blend. The addition of crystalline PEO has a remarkable effect on the mechanical properties of crosslinked PER. Tensile testing shows that the elongation at break first increases greatly and then decreases slightly, whereas the Young's modulus and the tensile strength first decrease and then increase slightly with increasing PEO content in the blends. The variation of tensile properties was considered to be due to both the plasticization effect and the crystallization effect of PEO in the blends. The impact strength remains almost unchanged with increasing PEO content in the blends studied. No dramatic decrease of thermal stability for PER/PEO blends was observed for the blends with PEO content up to 30 wt %.

1. Introduction

Studies of thermosetting polymers such as epoxy resins, unsaturated polyester resins and novolac resins and their blends have received increasing interest recently [1–5]. Unsaturated polyester resins (PER) have been widely used as the matrix of glass fibre reinforced composites [6], sheet-moulding and bulk-moulding compounds [7] due to their low manufacturing costs and high tensile strength. However, major drawbacks of PER, such as polymerization shrinkage [8], their inherent brittleness and low resistance to crack propagation due to the high degree of crosslinking [9, 10] have confined the application of PER to situations where the stress is relatively low and preferably static. Therefore, modification of PER is essential to meet industrial demands [11]. The inclusion of low profile additives such as poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) into PER may overcome the high polymerization shrinkage occurring during copolymerization of the unsaturated polyester resin with the crosslinking monomer [12–14]. Pattison *et al.* [12, 13] indicated that in either single-phase or two-phase unsaturated polyester resin blends, thermal expansion of styrene monomer in the early curing stage and stress-induced cracking in the later stage have important roles in the low profile and low shrink behaviour of these blends. Huang and Su studied the effect of low profile additive [14] and comonomer [15] on the curing kinetics of polyester resins in detail and found that intramicrogel and intermicrogel crosslinking reactions predominated the curing reaction in the early and later stage, respectively. As a successful routine of modification, the mechanical properties of PER can be improved through inclusion of reactive liquid rubbers to the system [16, 17]. Bucknall *et al.* investigated the morphology and properties of thermoset blends made

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from PER and PVAc [18]. They found that the change from particulate PVAc to a co-continuous structure was associated with a sharp drop in G_{IC} and K_{IC}, i.e. in and in the stress intensity factor.

The modification of thermosetting polymers by a compatible polymer has provoked much attention. We have reported our previous studies on poly(ethylene oxide) (PEO)/epoxy resin blends [19–21] and poly(ε-caprolactone)/novolac resin blends [22]. It was found that the miscibility and morphology of these thermosetting blends were remarkably affected by crosslinking. However, few investigations have been concerned with unsaturated polyester resin/crystalline polymer blends [4]. The results obtained by Mucha [4] indicate that blends of PER and PEO are miscible as evidenced by the appearance of a single, composition-dependent glass transition temperature. In the previous two papers [23, 24], we have also investigated PER/PEO blends by means of differential scanning calorimetry (DSC) and Fourier-transform infrared spectroscopy. It was found that hydrogen-bonding interaction between the hydroxyl groups of PER and the ether oxygen of PEO is the driving force for the miscibility of PER/PEO blends. The crosslinking of PER has a great influence on the crystallization behaviour of PEO in the blends. In this contribution, we report our studies of the phase behaviour, mechanical properties and thermal stability of PER/PEO blends. In particular, the effect of the addition of PEO on the mechanical properties of PER will be addressed in detail.

2. Experimental

2.1. Materials and preparation of samples

The poly(ethylene oxide) ($M_n = 21\,500$) was supplied by Farco Chemical Supplies, USA. The uncured unsaturated polyester resin (OERS) composed of 67 wt % oligoester resin (OER) ($M_n = 1000$) and 33 wt % styrene as a crosslinking monomer was supplied by Shanghai Institute of Synthetic Resins, Shanghai, China. The OER was a prepolymer of isophthalic acid (PA), fumaric acid (FA), and propylene-glycol (PG), with a molar ratio of PA/FA/PG = 1/1/2.2.

In order to prepare crosslinked PER/PEO blends, OERS and PEO were mixed at 70 °C to form a homogeneous clear liquid blend, then 1.5 wt % benzoyl peroxide of OERS was added to the blend with continuous stirring until a clear mixture was obtained (in approximately 3 min). The mixture was poured into a stainless steel mould and cured in an oven at 65 °C for 14 h, followed by successive postcuring at 90 °C for 3 h and at 120 °C for 3 h.

2.2. Dynamic mechanical analysis (DMA)

The dynamic mechanical tests were carried out on a dynamic mechanical thermal analyser Du Pont TA 2100 with a frequency at 1.0 Hz. The scan was performed at a heating rate of 3 $^\circ\mathrm{C\,min}^{-1}$ in tensile mode from 20 °C until the sample became too soft to be tested. The dimension of the specimen was $1.5 \times 1.0 \times 0.1$ cm.

2.3. Tensile tests

Tensile tests were carried out on a DSC-500 testing machine (Shimadzu Co. Ltd, Japan) at ambient temperature (25 °C). Standard dumbbell specimens (ASTM D638) with $2.5 \times 0.6 \times 0.4\ \mathrm{cm}^3$ neck were used. The crosshead speed was 2 mm min^{-1}, corresponding to a relative strain rate of 0.08 min^{-1}.

2.4. Impact tests

Notched Izod impact tests was done on an AFS/MK3-654S/000 Izod impact tester (CEAST Co., Germany) at 20 °C according to ASTM D256 standard. A minimum of five specimens with a notched angle of 45° were tested in all cases.

2.5. Thermogravimetric analysis (TGA)

A WRT-3 thermogravimetric analyser (Shanghai Instrumental Corp.) was used to investigate the thermal stability of the blends. The samples (about 10 mg) were heated under an air atmosphere from ambient temperature to 600 °C and at a heating rate of 10 $^\circ\mathrm{C\ min}^{-1}$ in all cases.

3. Results and discussion

3.1. Phase behaviour and dynamic mechanical properties

All the cured PER/PEO blends obtained were transparent just above the melting point of PEO. This observation primarily suggests that the system is miscible at the amorphous state, or no phase separation occurred at the scale exceeding the wavelength of visible light. When cooled to ambient temperature, the blends with more than 30 wt % PEO content became opaque. This was ascribed to the crystallization of PEO in the blends. All these PER/PEO blends were subjected to DMA measurement. The dynamic mechanical spectra of the PER/PEO blends are shown in Figs 1 and 2. It can be seen that the initial storage modulus, E', decreases regularly with PEO content up to 30 wt % in the blends, which may be the result of the plasticizing effect of PEO due to its low glass transition temperature, T_g. It is noted that E for the 60/40 and 40/60 PER/PEO blends increases dramatically compared with the 70/30 PER/PEO blend at low temperatures, and both of them are close to that for the 80/20 PER/PEO blend. The dramatic increase of E for the 60/40 and 40/60 PER/PEO blends can be considered to be due to the crystallization of large amounts of PEO in these blends. It is interesting to note from Fig. 2 that the single tan δ peak is rather asymmetric even for the pure PER. A similar phenomenon was also observed in polyurethane/unsaturated polyester interpenetrating polymer networks studied by Chou and Lee [25]. The asymmetry of tan δ for the PER/PEO blends remained unchanged with the addition of PEO. Much narrower peaks appeared for only the 60/40 and 40/60 PER/PEO blends, whereas relatively wider tan δ peaks were observed for the other blends. The T_g values can be obtained from the tan δ peaks in Fig. 2. Fig. 3 summarizes

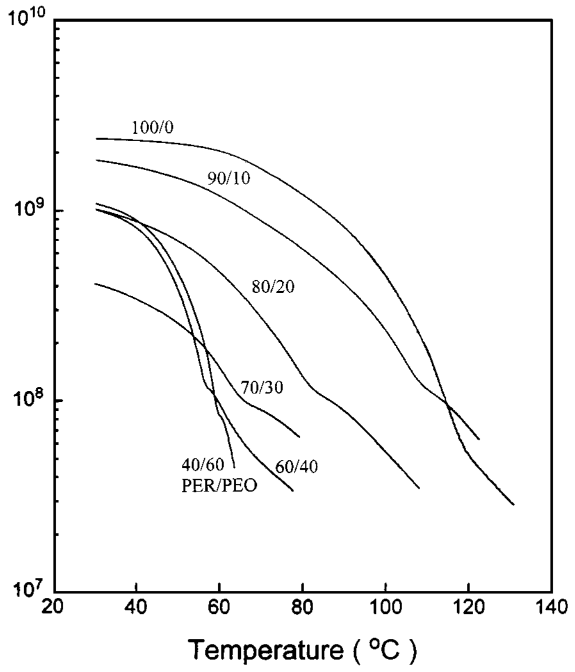

Figure 1 Storage modulus, E', versus temperature for PER/PEO blends.

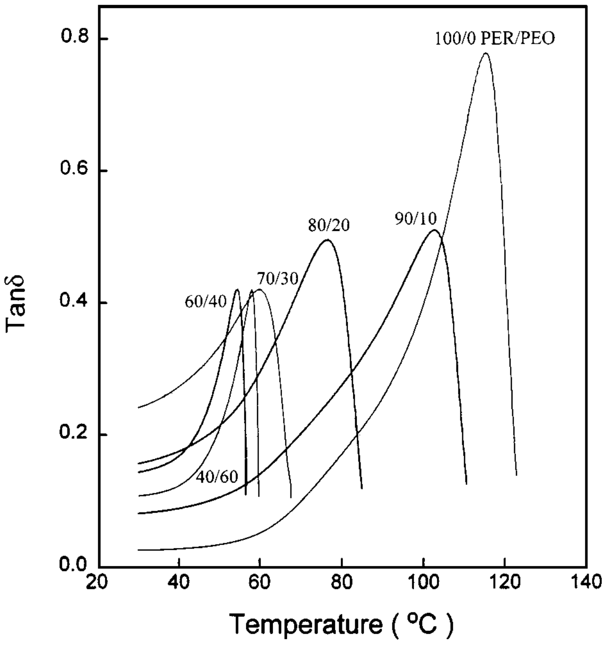

Figure 2 Tan δ versus temperature for PER/PEO blends.

the T_g values obtained as a function of blend composition. The T_g value of pure PEO used in Fig. 3 was taken from the dynamic mechanic spectra of PEO obtained by Robeson *et al.* [26]. The existence of single, composition-dependent T_g intermediate between those of the pure components suggests that PER/PEO blends are homogeneous in the amorphous phase, which verifies the conclusion we obtained previously by means of DSC [23]. This result is also in a good agreement with that obtained by Mucha [4].

It can be seen from Fig. 3 that the experimentally obtained T_g coincide quite well with the additivity of T_g of the two components when the PEO concentration is not more than 40 wt %. Herein, the T_g–composition relationship of the system is not necessarily described according to the empirical equations, such as the Fox [27] and Gordon-Taylor equations [28], which are generally used to depict miscible physically blended materials. In the present case, polymerization of the unsaturated polyester resin was initiated by radicals and some chain transferring reaction probably occurred between PER and PEO. Therefore, the resultant materials could include copolymers of PER and PEO. It is noted that the T_g of the 40/60 PER/PEO blend shows an obvious positive deviation from the additivity. The phenomenon is ascribed to the crystallinity of PEO. On the one hand, crystallization of PEO causes stiffening of the amorphous phase by reinforcement of PEO spherulites. On the other hand, the crystallization also gives rise to concentration of PER in the amorphous phase. Both the factors result in an additional increase in T_g. Similar phenomena were also seen for other miscible amorphous/crystalline polymer blend systems [19, 20, 29–31].

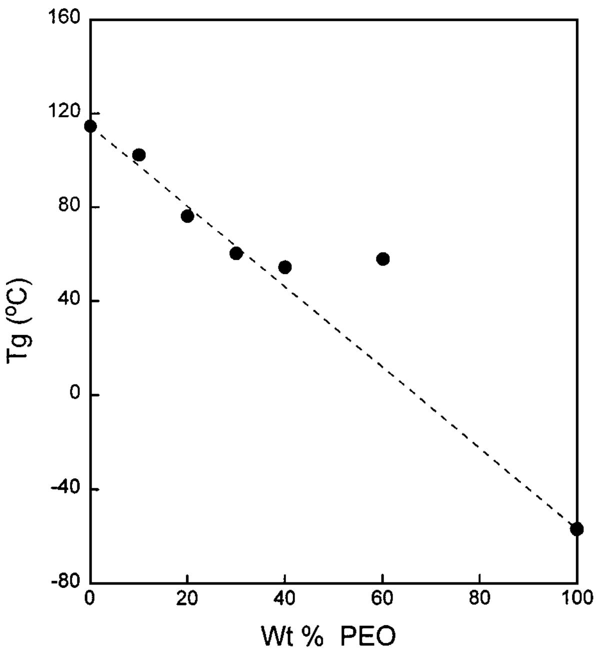

Figure 3 Composition dependence of glass transition temperature, T_g, of PER/PEO blends. The dashed line is the T_g additivity of the two components. The T_g value of pure PEO was taken from the dynamic mechanic spectra of PEO obtained by Robeson *et al.* [26].

3.2. Tensile properties

The modification of unsaturated polyester resins by means of physical blending or chemical modification have been previously reported [32–36]. These modifiers included other polymers [32, 33], rigid fillers [35] and soft fillers [36]. These approaches produced polymers and composites with different mechanical properties. Usually, the toughening of crosslinked PER by blending with various polymers involves a process of dissolving the polymer in the precursor of PER, i.e. OERS prior to curing and allowing phase separation to occur to different degrees. Reports of single phase unsaturated polyester resin blends are rarely seen in the literature. So it is interesting to investigate the mechanical properties of miscible PER/PEO blends in detail.

The stress–strain curves of the PER/PEO blends are shown in Fig. 4. In general, there is a linear increase of

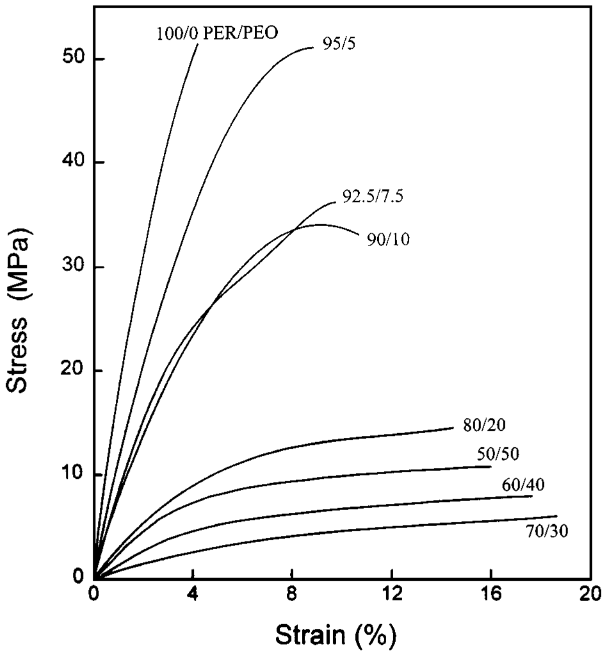

Figure 4 Stress–strain diagrams for PER/PEO blends.

stress with strain up to some degree. For pure PER, an obvious brittle fracture was observed. The stress–strain curve is almost linear till the fracture point is reached. With increasing PEO content in the blends, the curve slants to the right, indicating that the blends show some ductility and yield behaviour becomes more apparent. The tensile strength first decreases rapidly with PEO content up to 30 wt %, then it increases slightly with further increase of PEO content in the blends. For the 95/5 PER/PEO blend, the decrease of tensile strength is not very large, but the blend shows yield behaviour and the elongation at break doubles compared with that for pure PER. Rubber-like behaviour was observed for the 70/30 PER/PEO blend. It can be seen from Fig. 4 that the 95/5 PER/PEO blend has ideal tensile properties in comparison with other blend compositions.

Fig. 5 shows the change of elongation at break with PEO content in PER/PEO blends. Pure PER is very brittle, with only 3.0% elongation at break. PEO modification greatly improves this situation; some samples in Fig. 5 show elongation at break exceeding 18%. With the addition of PEO to the blends, the elongation at break first dramatically increases to 18%, then decreases slightly. Thus, the incorporation of PEO in PER converted the very brittle materials to a quite ductile material. PEO, due to its low T_g, can be considered as a polymeric plasticizer of amorphous (glassy) thermosetting PER resin. Conventional low molecular weight plasticizers (usually called monomeric) may improve the flexibility of a resin, but often exhibit undesirable performance flaws (volatility, migration, extractability, etc.). A polymeric plasticizer provides flexibility to the resin, may improve the workability, and provides a marked increase in performance over its monomeric counterpart. As indicated previously, a major drawback of PER is its brittleness and poor resistance to crack propagation; the discovery of the PEO plasticization effect for PER may be important in increasing the ductility of PER in practical uses.

The marked increase in ductility, however, is accompanied by a loss of Young's modulus and tensile strength as shown in Figs 6 and 7, respectively. It can be seen that both the Young's modulus and the tensile strength decrease remarkably at first with a PEO content up to 30 wt %, and then increase slightly. The tendency of Young's modulus to vary for the blends is in accordance with variation of the dynamic storage modulus. With increasing PEO content in the blends, the change of modulus is considered to be the overall result of both the plasticization and crystallization effects of PEO as discussed previously. Martuscelli and coworkers attempted to modify commercial liquid rubbers chemically to enhance their reactivity towards a PER matrix, which was considered to be one of the most successful modifications. They transformed a hydroxyl-terminated polybutadiene into an isocyanate-terminated rubber and the isocyanate functionalities were reacted with the hydroxyl end groups of PER resins prior to the curing process [16]. They also made

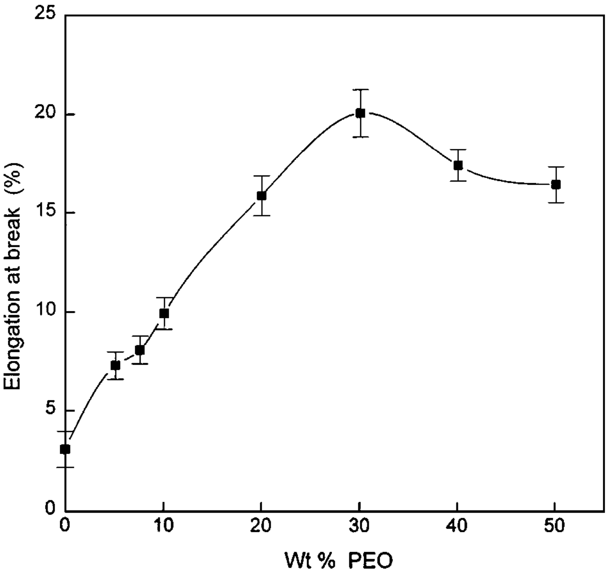

Figure 5 Elongation at break as a function of PEO content for PER/PEO blends.

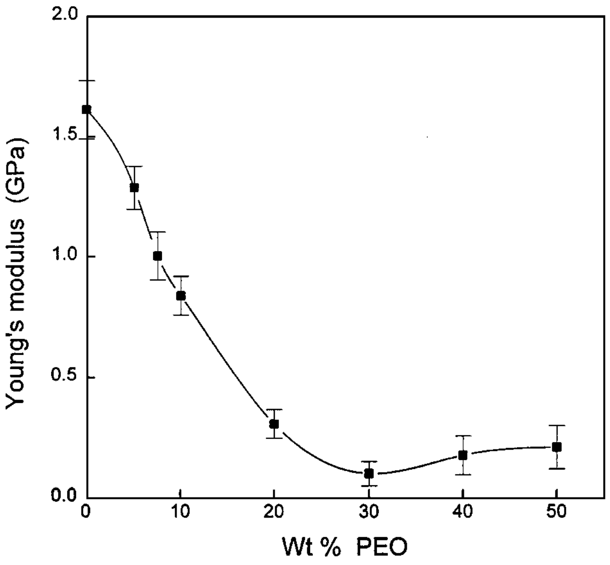

Figure 6 Young's modulus as a function of PEO content for PER/PEO blends.

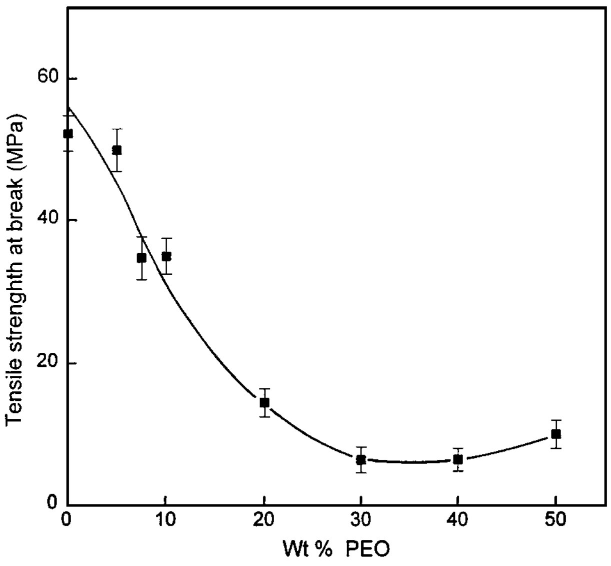

Figure 7 Tensile strength as a function of PEO content for PER/PEO blends.

a polyisobutylene (PIB) having olefinic end groups to react with maleic anhydride to obtain PIB bearing anhydride functionalities [17]. Considerable enhancement of toughness was achieved when modified rubbers were used in place of the plain polybutadiene or PIB. Since the method of chemically modifying commercial liquid rubbers requires strict synthetic reaction, it is not realistic for commercial uses. Although homogeneous PER/PEO blends have several mechanical advantages, they do not demand any complex synthetic methods. It is known that PEO dissolved in PER precursor, i.e. OERS, very easily prior to curing, so crosslinked PER/PEO blends may show potentially commercial values.

3.3. Impact strength

The effect of PEO on the impact strength of PER/PEO blends is given in Fig. 8. As can be seen, with increasing PEO content, the impact strength first increases slightly to the highest value then decreases to a level and remains almost invariant. There are two aspects that may affect the impact strength of PER/PEO blends. With increasing PEO content, firstly, the decrease of strength will cause the decrease of impact strength, secondly, the increase of ductility will cause the increase of impact strength. The tendency for the impact strength to vary with PEO content is the total result of the above two effects. The slight increase of impact strength for the 95/5 PER/PEO blend may be due to the fact that the tensile strength decreases slightly, but the elongation at break increases relatively largely.

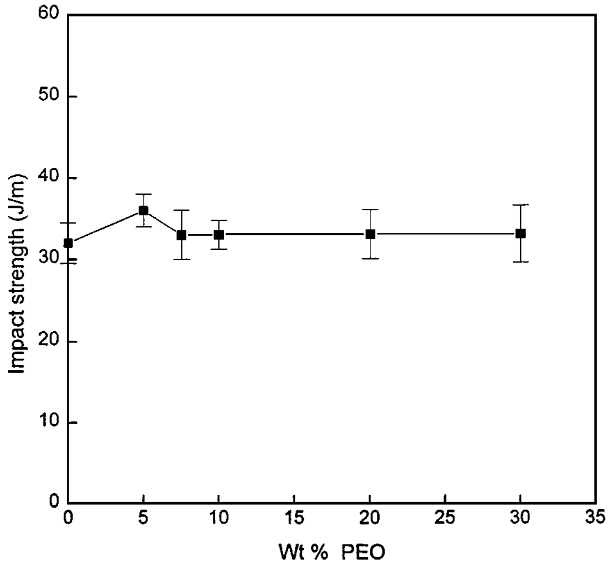

Figure 8 Impact strength as a function of PEO content for PER/PEO blends.

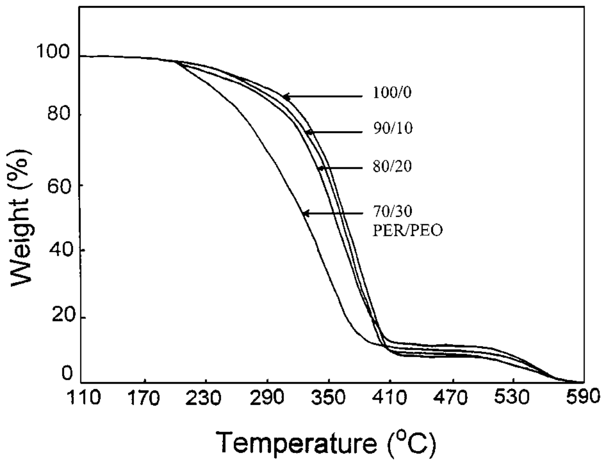

Figure 9 TGA curves for PER/PEO blends heated at 10 °C min^{-1} in air.

3.4. Thermal stability

TGA was applied to investigate the thermal stability of the blends. Fig. 9 shows the TGA curves recorded in air. It can be seen that pure PER and all the blends investigated exhibit a two-step weight loss mechanism, among which the first step is the dominant weight loss process. The TGA curves shifted towards low temperature with increasing PEO content in the blends. The curves are quite close for the pure PER, 90/10 and 80/20 PER/PEO blends; whereas for the 70/30 PER/PEO blend the TGA curve is shifted to the low temperature dramatically. It can be considered that no dramatic decrease of thermal stability for PER/PEO blends is observed for blends with a PEO content up to 30 wt %.

4. Conclusions

The DMA studies show that PER/PEO blends have a composition dependent T_g and are homogenous in the amorphous state. The initial dynamic storage modulus, E', decreases with PEO content up to 30 wt % in the blends, whereas E for both the 60/40 and 40/60 PER/PEO blends is close to that for the 80/20 PER/PEO blend and much larger than that for the 70/30 PER/PEO blend. The addition of PEO has a remarkable plasticizing effect on crosslinked PER due to the low T_g value of PEO. Crystallization of PEO in the blends also has a considerable influence on the mechanical properties. With increasing PEO content in the blends, the elongation at break first increases greatly, and then decreases slightly; whereas both the Young's modulus and the tensile strength first decrease remarkably and then increase slightly. The impact strength remains almost unchanged with increasing PEO content in the blends. No dramatic decrease of thermal stability for PER/PEO blends is observed for blends with a PEO content up to 30 wt %.

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