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Thermal decomposition of miscible phenoxy/poly(ethylene oxide) blends

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The thermal decomposition of miscible blends composed by the poly(hydroxy ether of bisphenol A) (phenoxy) and poly(ethylene oxide) (PEO) has been investigated by dynamic thermogravimetric analysis. The results obtained indicate that the blend composition affects the thermal decomposition processes. In general it can be seen that phenoxy causes a negative effect on the thermal stability of the blends.

1. Introduction

Polymer blends composed of poly(hydroxy ether of bisphenol A) (phenoxy) and poly(ethylene oxide) (PEO) have been studied by Robeson *et al.* [1] and recognized as miscible as judged by the emergence of a single glass transition temperature, intermediate to that of the pure components, in the whole composition range. On the other hand, it was also observed [1] that different properties of the blends, such as the crystallization rate and the degree of crystallinity of PEO in the blends are influenced by the blend composition.

An important aspect of the polymer blends is their thermal stability. The reason is that the preparation of such mixtures generally requires processing techniques in which the polymers are subjected to high temperatures.

It has been reported [2, 3] that the miscibility level should influence the thermal stability of the blend, and particularly, in miscible blends, in which the polymers are intimately mixed in a microscale, an interaction between them during the thermal decomposition process should be present.

In this work, we have studied miscible phenoxy/PEO blends in an attempt to determine the influence that each polymer has on the thermal stability of the other. We have used dynamic thermogravimetric analysis to obtain the different parameters involved in the thermal degradation processes.

2. Experimental details

The polymers used in this work were commercial products. Phenoxy (PKHH, Union Carbide) was obtained from Quimidroga S.A., Barcelona, Spain. Their average molecular weights were determined by GPC in THF at 30° C. The results obtained were $M_w = 50\,700$ and $M_n = 18\,000$. PEO was obtained from Polysciences. Its average viscosity molecular weight, $M_v = 365\,000$ was obtained in benzene at 25° C, using the equation [4].

$$[\eta] = 3.97 \times 10^{-4} M_v^{0.686}$$

Phenoxy/PEO blends in different compositions were prepared by casting, using dioxane as the solvent. The solvent evaporation was conducted at room temperature under a stream of air. The resulting films were dried in vacuo until a constant weight was reached.

The miscibility of the blends was investigated by measuring their glass transition temperature (T_g) on samples which had been quenched previously in liquid nitrogen from the melt state. A Perkin Elmer DSC-2 differential scanning calorimeter was used, at a heating rate of $40\,\mathrm{K\,min^{-1}}$. The glass transition temperatures were determined in the usual manner.

The thermal decomposition of phenoxy/PEO blends was studied by dynamic thermogravimetric analysis in a nitrogen atmosphere. A Dupont 951 thermobalance attached to a Dupont 990 module was used. The heating rate was $10°\,\mathrm{C\,min^{-1}}$. Other details have been given in previous papers [5, 6].

3. Results and discussion

Results obtained previously have shown that phenoxy and PEO are two miscible polymers. Thus Robeson *et al.*, [1] have found a single glass transition temperature in phenoxy/PEO quenched samples as well as in annealed samples.

We have also found a single T_g in all the compositions

TABLE I Glass transition temperatures (K) for Phenoxy/PEO blends

Composition (Phenoxy/PEO)	This work quenched	Robeson *et al.* quenched	Robeson *et al.* annealed
0/100	230	–	216
10/90	243	–	–
15/85	–	–	283
20/80	235	–	–
25/75	–	226	293
30/70	238	–	–
35/65	–	236	307
40/60	245	246	309
45/55	–	248	316
50/50	240	257	318
55/45	–	268	316
60/40	232	279	313
65/35	–	288	312
70/30	266	297	–
80/20	272	319	–
90/10	287	339	–
100/0	368	369	–

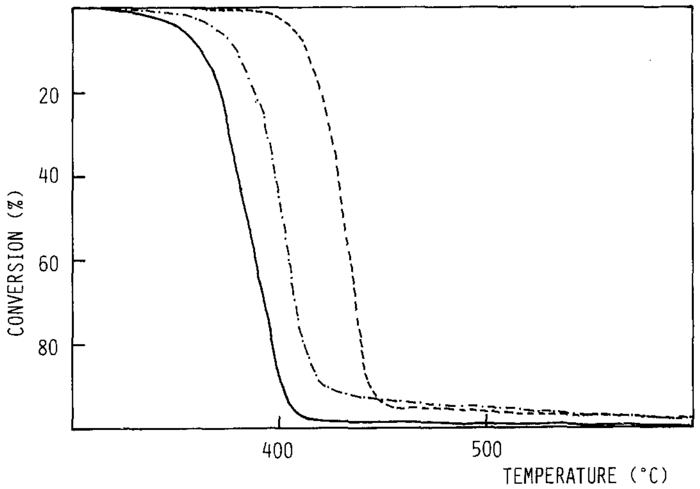

Figure 1 Thermograms for phenoxy (– – –), PEO (——) and phenoxy/PEO (50/50) blend (–·–·–).

of phenoxy/PEO blends investigated. However, the T_g–composition relationship that we have obtained is very different from that obtained by Robeson *et al.* for quenched and annealed samples, as can be observed in Table I. The T_g values obtained by Robeson are higher for annealed samples, as could be expected as a consequence of the PEO crystallization, which produces a decrease in the PEO concentration in the amorphous phase. If we look at the results corresponding to quenched samples, it is clear that our T_g values are lower than those obtained by Robeson at low PEO contents, whereas at high PEO concentration we have found higher T_g values. The differences observed can be explained if we take into account that two very different molecular weights of PEO have been used in both works. On the other hand, the cooling rates may be different in our work and in that of Robeson *et al.*, although in both cases a quenching to liquid nitrogen temperature has been carried out. These two factors can influence the PEO crystallinity to a great extent and hence the PEO concentration in the amorphous phase, giving rise to different T_g values. Finally, the experimental techniques used to determine the glass transition temperatures are different in the two works, and this may also influence the T_g values.

In spite of the differences observed, the two works, that of Robeson *et al.*, and our work, indicate the miscibility of phenoxy/PEO blends, which has been attributed to the formation of hydrogen bonding interactions between the lateral hydroxyl groups of phenoxy and the ether groups of PEO.

In the second stage, and as has been already mentioned in the introduction, we have studied the thermal decomposition of the blends, in an attempt to determine the influence that each polymer has on the thermal stability of the other.

In Fig. 1 we show the thermograms corresponding to the thermal decomposition of pure phenoxy and PEO and a phenoxy/PEO (50/50) blend. As can be observed, both pure polymers decompose in a single stage. If we compare the thermal stability of the polymers, it is clear that phenoxy is more stable than PEO. Thus phenoxy decomposes at higher temperatures and, as an example, the T_i (initial decomposition temperature) for PEO is 320° C, whereas for phenoxy it is 360° C. The thermogram for the phenoxy/PEO (50/50) blend indicates that this blend has an intermediate thermal stability between those of phenoxy and PEO. On the basis of the experimental thermograms we have obtained two characteristic temperatures of the thermal degradation processes. These are T_i, which has been defined before, and T_{50}, defined as that temperature at which 50 wt % of the sample has

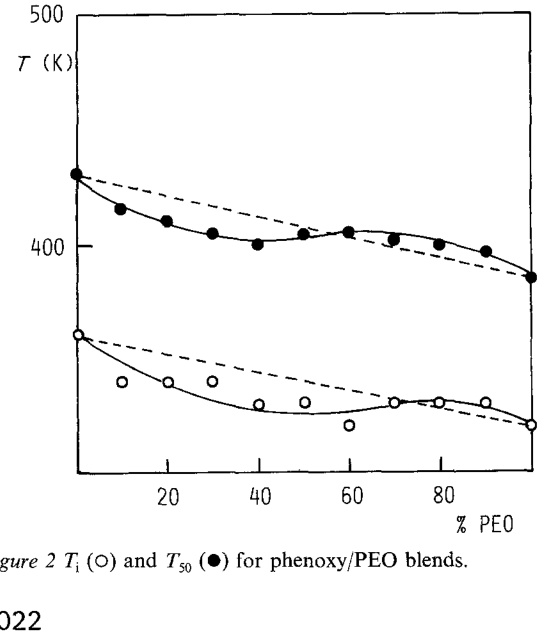

Figure 2 T_i (○) and T_{50} (●) for phenoxy/PEO blends.

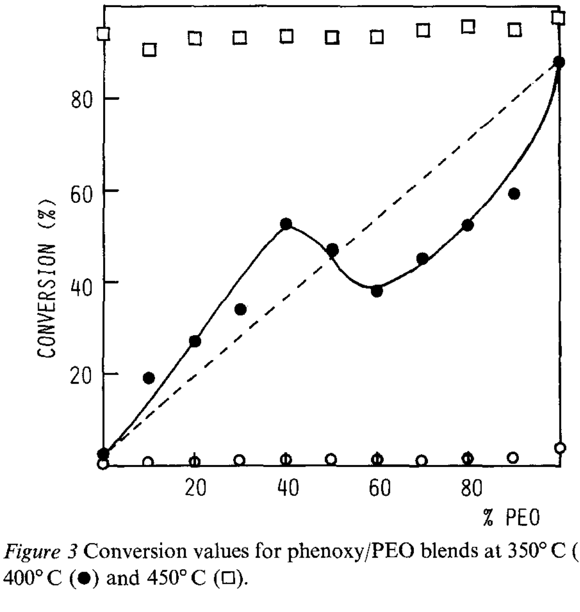

Figure 3 Conversion values for phenoxy/PEO blends at 350° C (○), 400° C (●) and 450° C (□).

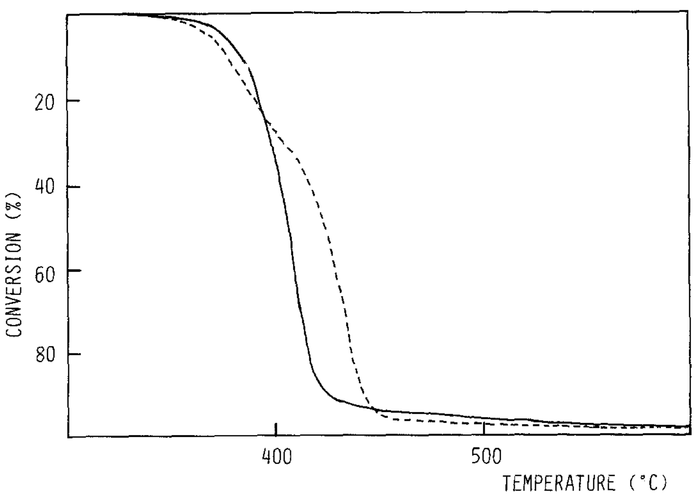

Figure 4 Experimental (——) and theoretical (- - -) thermograms for phenoxy/PEO (70/30) blend.

decomposed. These characteristic temperatures are shown in Fig. 2 as a function of the blend composition.

If we look at the T_i values, it appears that these are generally intermediate to those of the pure components. A comparison of the experimental T_i values with those obtained by applying the additivity rule to values corresponding to the pure components seems to indicate that at PEO contents lower than approximately 75 wt %, a destabilization effect is present in the blends, whereas at PEO contents higher than the above mentioned, a slight stabilization effect is observed. Similarly, the T_{50} values indicate a destabilization of the blends when the PEO content is lower than 50% and a stabilization effect at higher PEO concentration.

The existence of stabilization and destabilization effects, as described above, may be corroborated if we examine the conversion values obtained at different temperatures in the experimental thermograms. In Fig. 3, the conversion data at 350, 400 and 450° C have been plotted as a function of the blend composition. It can be observed that, at 350° C, the conversion values are very low and the greater the PEO content in the blend, the greater these values tend to be. On the other hand, at 450° C, the conversion values are approximately 100 wt %, irrespective of the blend composition, which indicates that the decomposition processes are already in the final stages. A more interesting behaviour is found in the conversion data obtained at 400° C. This temperature corresponds approximately to the intermediate stages in the thermal decomposition, as can be observed in Fig. 1. In the conversion–composition relationships obtained at 400° C, it can be seen that when the PEO concentration in the blend is lower whan 50%, the conversion values obtained experimentally are higher than those obtained by addition from the values corresponding to pure components. Thus, it appears that such blends with low PEO content decompose more rapidly than expected and are destabilized. This result is in good agreement with that obtained from the T_{50} values. An opposite behaviour is obtained for blends with PEO contents higher than 50 wt %. These blends appear to be stabilized from conversion data, which is in good agreement with the T_{50} data.

Figs 4–6 show a comparison between the experimental thermograms and those obtained by addition from the data corresponding to pure components. These figures correspond to phenoxy/PEO (70/30, 50/50 and 30/70) blends. As can be observed, three different stages exist. In the first stage, in the low temperature range, the experimental conversion at a given temperature is lower than that calculated by means of the additivity rule. This indicates that in this low temperature range, the blends are stabilized, this effect being greater when the PEO content in the blend is greater. In the second stage, the experimental conversion at a given temperature is higher than the theoretical one, indicating a stabilization effect. Finally, at temperatures higher than 440° C, the experimental conversion is lower than that obtained theoretically, indicating a stabilization of the blends. However, the

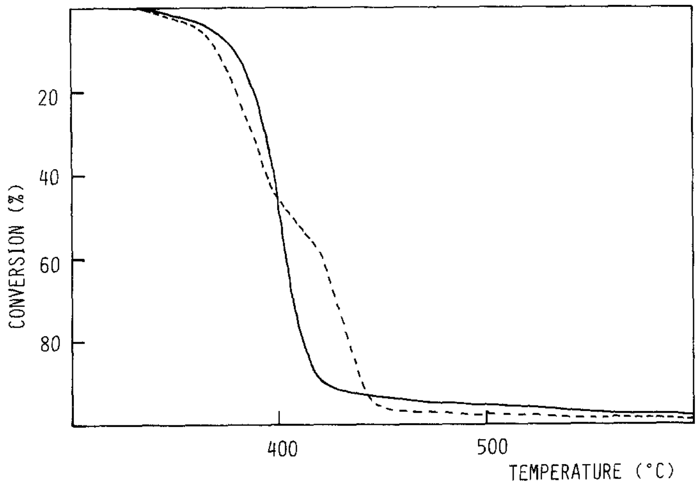

Figure 5 Experimental (——) and theoretical (- - -) thermograms for phenoxy/PEO (50/50) blend.

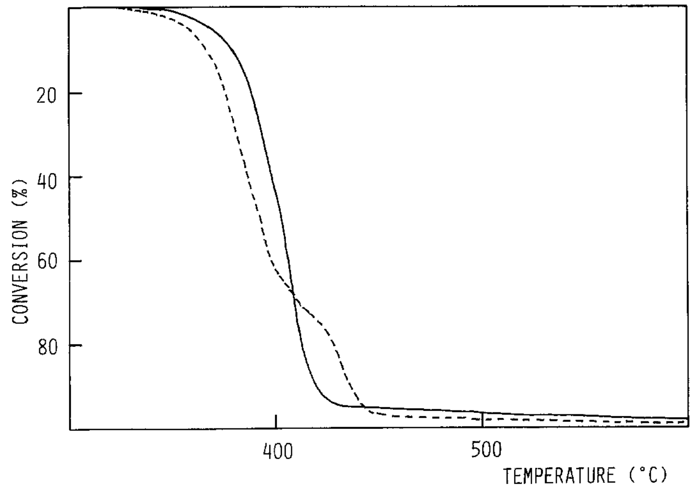

Figure 6 Experimental (——) and theoretical (- - -) thermograms for phenoxy/PEO (30/70) blend.

differences between the experimental and theoretical conversions are slight in this third stage.

All the results presented here indicate clearly the existence of an influence of the blend composition on the thermal degradation processes of phenoxy/PEO blends. It appears that, in the first stages, phenoxy destabilizes the blends, and the greater the phenoxy content, the greater the destabilization effect. On the contrary, at high PEO contents, a stabilization effect can be seen. At higher temperatures, the main effect observed is a destabilization effect, which is present in all the compositions studied. Thus, our results show that although phenoxy is more stable than PEO, the first polymer destabilizes the mixtures. Similar results were found in phenoxy/PET and phenoxy/PBT blends [3].

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