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A study of the degradation of uncured DGEBA/PVP blends by thermogravimetry and their miscibility state*

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Poly(*N*-vinyl pyrrolidone) was blended with an epoxy resin to give a miscible blend. The thermal stability of DGEBA/PVP blends was studied by dynamic thermogravimetry. The kinetic parameters of the degradation were calculated. The results indicated that the presence of one component influences the stability of the other. In general, PVP has a stabilizing effect on DGEBA, but PVP is destabilized by DGEBA. The chemical interactions between PVP and DGEBA on the one hand, and the viscosity of the medium, on the other hand, seem to be the factors governing the degradation behavior of the blend.

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1. Introduction

Epoxies are a class of thermosetting resins widely used as matrices for composites in structural applications. They have excellent chemical and electrical resistance and good mechanical properties, together with high thermal stability. However, an important limitation of epoxy resins is their inherent brittleness arising from their cross-linked structure. In order to improve their poor fracture toughness, epoxies have often been modified by the incorporation of rubbers [1]. Unfortunately, although the impact resistance is improved, both the resin modulus and the end-use temperature are reduced.

In recent years, ductile engineering thermoplastics have been developed with a high glass transition temperature, T_g, such as polyether sulphone [2, 3], functionalized polysulphones [4, 5], polycarbonate [6–9], polyetherimide [10, 11], polyimide [6, 12, 13], polyphenylene oxide [14], phenoxy resins [15], etc. The thermoplastic is soluble in the uncured resin and phase separates during the curing process. However, whether the addition of the thermoplastic to an epoxy in a blend will result in the alteration of the thermal stability of the resin is not yet clear. The thermoplastic might deteriorate the resistance of epoxy at high temperatures, thus limiting the potential applications of the modified resin. Several papers have been published concerning the degradation of polymer blends [16–21], but no articles have been found dealing with the high temperature degradation behavior of epoxy/thermoplastic blends. Therefore, it was thought interesting to analyze the effect that the addition of poly(N-vinyl pyrrolidone), PVP, a thermoplastic modifier of high T_g, has on the thermal stability of an epoxy resin. PVP is a water-soluble polymer, miscible with many polymers, which is capable of specific interactions, including hydrogen and dipolar bonding at the imido group [22].

The objective of this paper is to study the thermal stability of uncured epoxy/PVP blends with a kinetic treatment of the degradation results. The study of the kinetics of degradation for cured epoxy systems is in progress and will be communicated shortly.

2. Experimental

The epoxy resin used in this work was the diglycidyl ether of bisphenol-A (DGEBA), DER 332, a low molecular weight crystalline solid from Dow Chemical, kindly supplied by Quimidroga (Spain). It had a measured epoxy equivalent weight of 175. The poly(N-vinyl pyrrolidone) (PVP) was purchased from Sigma (PVP-360, $Mw = 360{,}000$). Because of the very hygroscopic nature of PVP, it was dried in vacuum at 100 °C overnight and kept in a dessicator until used. DGEBA/PVP blends in different compositions were prepared by dissolving weighed amounts of both polymers in methylene chloride, to give a 2% (w/v) solution. Solvent was then eliminated by placing the solution under an infrared lamp and drying under vacuum at 80 °C for 1 day. Blends containing more than 80% PVP were dried at 100 °C under vacuum for an additional day.

The calorimetric measurements were made in a dry nitrogen atmosphere in a Perkin-Elmer DSC-2 differential scanning calorimeter equipped with an intracooler for below ambient temperature measurements. The instrument was calibrated with an indium standard. Two

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runs at 20 K/min between 240 and 473 K were performed on each sample. The sample weight used in the DSC cell was about 7 mg. The T_g was measured on the second scan as the intersection of the tangent to the base line before the transition and the straight line of maximum slope encountered during the transition.

Dynamic Thermogravimetric analyses were carried out with a Du Pont 951 module coupled to a 2000 Thermal Analyst. A heating rate of 10 °C/min and a nitrogen flow rate of 50 ml/min were used. The sample weight was about 7 mg.

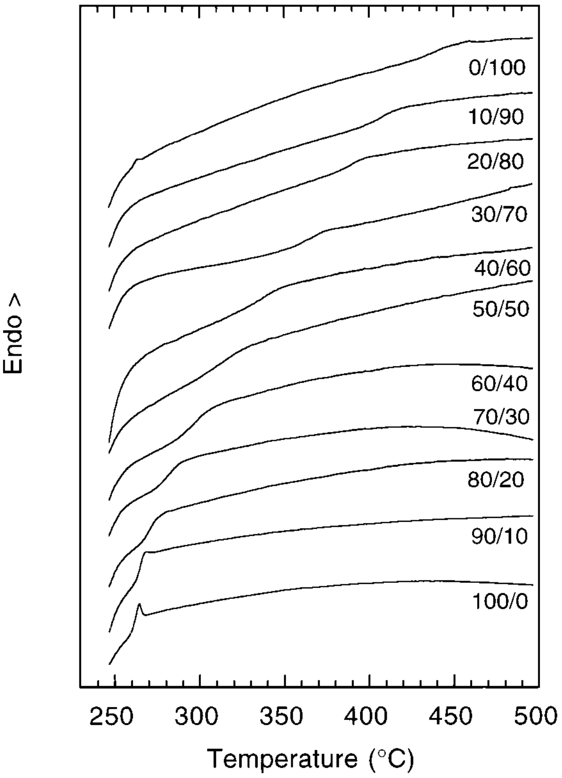

Figure 1 Original DSC traces of DGEBA/PVP blends. Curves for the different compositions have been shifted vertically.

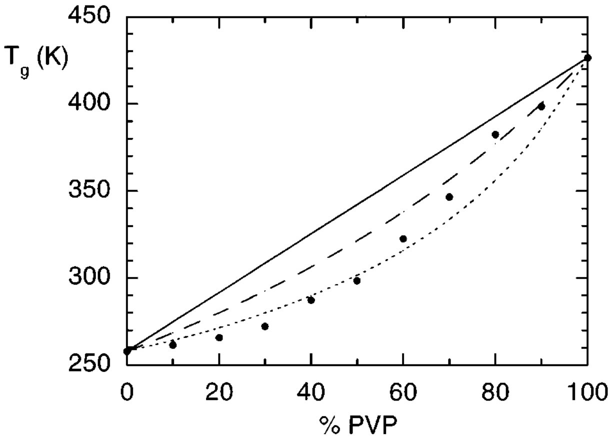

Figure 2 T_g vs. PVP content of DGEBA/PVP blends. —— linear additivity law, – – – Fox equation, and - - - - - Gordon-Taylor equation.

3. Results and discussion

All the uncured DGEBA/PVP blends were transparent. This is a good indication that monomer DGEBA might be miscible with PVP. The miscibility of these blends was ascertained by DSC T_g measurements. In Fig. 1, the original DSC traces for the DGEBA/PVP samples are shown. As can be seen, all blends show a unique T_g changing with composition. This behavior confirms the miscibility of this system. Usually, favourable interactions between the components are necessary for a blend to be miscible. The miscibility of PVP with DGEBA could arise from dipole-dipole interactions between the amido group of PVP and the oxirane groups of DGEBA. However, taking into account the low molecular weight of DGEBA, miscibility in this system could also be due only to entropic factors. In fact, uncured DGEBA has been observed to be miscible with many thermoplastics [23–25], but the blend phase separates when the molecular weight increases during the curing of the resin. In Fig. 2, a plot of the T_g vs. PVP content of DGEBA/PVP samples is shown. From the plot, it is evident that all the experimental values fall well under the straight line representing the linear additivity rule. Likewise, excepting the PVP-rich compositions, the experimental data are lower than those predicted by the Fox [26] equation. These two equations have often been used to predict the limiting values of T_g in miscible blends. However, our measurements are not well predicted by either of these theoretical expressions. It has been observed that the T_g-composition curves of many PVP-containing blends [27] can be fitted by the Gordon-Taylor equation [28]:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}$$

where T_{gi} and w_i are the T_g and weight fraction of polymer i, respectively; the subindices 1 and 2 refer to the component with lower and higher glass transition temperature, respectively; and k is an adjustable parameter that has been suggested to be related to the interaction strength between the components. The larger the k value is, the stronger the specific interactions are. The T_g-composition curve of the miscible DGEBA/PVP blend can be more satisfactorily described by the Gordon-Taylor equation with $k = 0.35$. This k is the value obtained by a least squares analysis of the linearized Gordon-Taylor expression to give the best fit of the experimental data. Similar k values have been reported for miscible blends showing a concave T_g-composition plot [27, 29–31].

Primary thermograms of dynamic TGA of DGEBA, PVP and their blends are shown in Fig. 3. Evidently, DGEBA appears to be more thermally unstable than PVP and totally volatilizes in a single stage at temperatures lower than 300 °C. Several authors have studied the mechanism of thermal degradation of DGEBA [32–35]. Neiman *et al.* [32] proposed that one of the main steps in the mechanism of decomposition consisted initially in the bond scission to produce a radical containing an intact epoxy group which subsequently isomerized to a radical containing a carbonyl group. This idea was also supported by Anderson [33], based on differential thermometric experiments, to account for the exothermic reaction observed during the thermal degradation of epoxy resins. However, the degradation

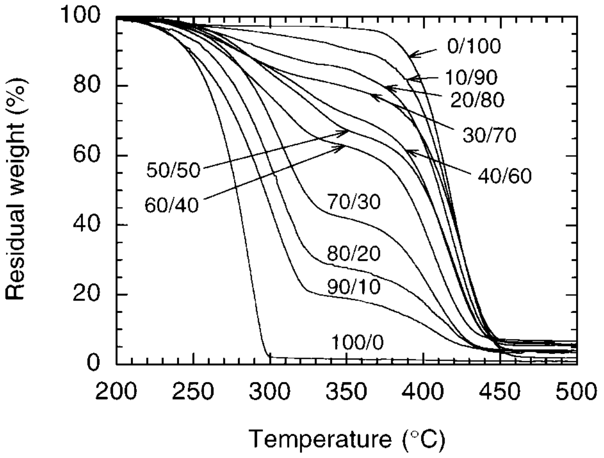

Figure 3 Percentage weight loss vs. PVP content of DGEBA/PVP blends by TGA.

scheme proposed by Neiman was found to be inadequate to explain the presence of the predominant phenolic compounds obtained during the thermal degradation of epoxy resins. Thus, Lee [34, 35] proposed that the thermal degradation of epoxy resins proceeded along several concurrent schemes. The isomerization process proposed by Anderson was one of the degradation schemes to which Lee added two major and one minor scheme. The first scheme was the homolytic cleavage of the bisphenol-A unit to yield isopropylphenol, ethyl-phenols, cresols and phenol. The second scheme was the heterolytic cleavage of the bisphenol-A unit to yield isopropenylphenol and phenol. The third scheme was postulated to be the cyclization of the glycidyl ether side chain to yield C_6H_5-O-C_3H_3 or C_6H_4-O-C_3H_4. In addition, during the pyrolysis of the DGEBA, some distillation of the uncured resin can be produced. The unpyrolyzed resin remains as part of the high boiling point volatiles, thus hindering the study of its thermal stability [35].

With respect to the PVP, it degrades mainly between 370 and 450 °C. Also, in the vicinity of 200 °C, a small weight loss of about 4% takes place. We have observed that by heating the PVP at 200 °C for 30 minutes, it acquires a slight brown tonality and becomes insoluble in water, thus revealing that some kind of cross-linking has taken place.

It is known that aqueous PVP is permanently gelled when cross-linked by reaction with certain chemical reagents [36], such as strong alkali, inorganic persulfates or peroxides [37]. Gelation with alkali involves the opening of the pyrrolidone ring to form poly(vinyl aminobutyric acid) units [38]. In the case of persulfate cross-linked gels, the mechanism of linkage seems to involve the abstraction of an hydrogen atom from the ring or vinyl group with the subsequent formation of a cross-link at this site [36]. Gels are also formed by γ-radiation and by ultraviolet irradiation of aqueous PVP solutions. Also, in these cases, the mechanism seems to proceed via the formation of free radicals. A gel results when radicals undergo intermolecular cross-linking [39]. All the above results suggest that, similarly, a free radical mechanism might be responsible of the insolubilization of PVP heated at 200 °C.

Other reactions in addition to cross-linking are possible. The macroradical may rearrange to a more stable state by chain scission, by disproportionation in the neighbourhood of the unpaired electron [36]. If this disproportionation occurs near the end of the chain, few volatile small fragments of low molecular weight are formed. The volatilization of these fragments could, possibly, explain the small weight loss observed around 200 °C.

The thermogravimetric curves of various DGEBA/PVP blends are also shown in Fig. 3. It is immediately apparent that all blends decompose in two stages, one in the region of the temperature at which DGEBA degraded, and the other at temperatures near the main decomposition stage of PVP. The TGA curves of all blend compositions lie between those of the homopolymers. Furthermore, the weight loss of the lowest temperature step decreases while that of the highest temperature increases with the PVP content. Thus, the low temperature degradation step in blends was assigned to the degradation of DGEBA, and the high temperature step to the degradation of PVP in the blends. Looking in more detail at the 40/60, 50/50 and 60/40 blends, more degradation stages can be detected which are more clearly revealed in the derivative thermogravimetric, DTG, curves shown in Fig. 4. In fact, in these compositions the first step of degradation shows two peaks in the DTG curve, named DER 1 and DER 2, while all the other blends show only one peak in this region, labelled DER. The peak relative to the PVP degradation has been labelled PVP.

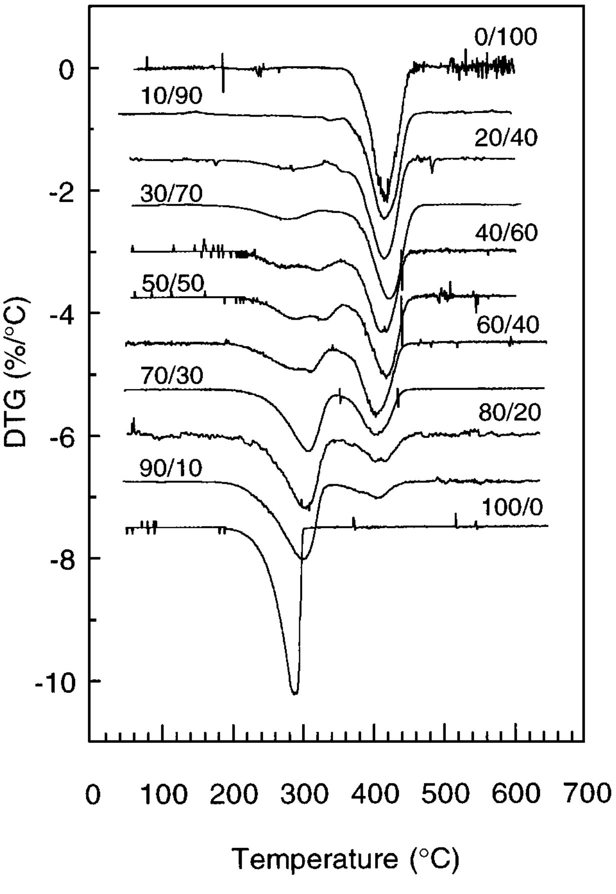

Figure 4 DTG curves of DGEBA/PVP blends. Curves for the different compositions have been shifted vertically.

TABLE I T_i and T_{max} for DGEBA/PVP blends

DGEBA/PVP	T_i(°C)	Stage in degradation	T_{max}(°C)
100/0	182	DER	289
90/10	180	DER	299
		PVP	403
80/20	180	DER	299
		PVP	404
70/30	190	DER	309
		PVP	403
60/40	200	DER 1	293
		DER 2	312
		PVP	404
50/50	213	DER 1	291
		DER 2	330
		PVP	419
40/60	212	DER 1	278
		DER 2	324
		PVP	419
30/70	189	DER	283
		PVP	423
20/80	181	DER	288
		PVP	417
10/90	180	DER	339
		PVP	417
0/100	181	PVP[a]	239
		PVP	421

[a]This peak corresponds to the cross-linking of PVP and is not the main degradation stage of PVP.

On the basis of the experimental thermograms two characteristic temperatures of the thermal degradation process were obtained. These are T_i, the initial decomposition temperature of the sample, and T_{max}, the temperature of maximum decomposition rate of each step. These values are reported in Table I. As shown in this Table, the addition of PVP to DGEBA produces a continuous increase in the initial decomposition temperature, reaching a maximum at the 50/50 blend. Additional amounts of PVP, however, cause a drop in T_i for PVP rich blends. The most stable composition, considered as the one with the highest T_i, seems to be that in which DGEBA and PVP are present in similar proportions.

With respect to the temperature of maximum rate of weight loss, for the lowest temperature degradation stage, similarly to the behavior observed in T_i, blends with PVP contents increasing from 0 to 30% show a steady rise in T_{max} from 289 to 309 °C. However, for samples with 40, 50 and 60% PVP, as mentioned before, the low-temperature degradation stage splits into two peaks whose T_{max} are lower and higher than that of the 70/30 blend. Finally, for blends richer than 60% in PVP, only one T_{max} is observed again. On the other hand, for the high temperature degradation stage, T_{max} generally decreases as the PVP content in the blend decreases. These results seem to indicate that, in this miscible blend, PVP has a positive influence on the thermal stability of DGEBA, mainly observed in DGEBA-rich blends, but, on the contrary, PVP is generally destabilized by DGEBA. Several papers have discussed the effect of miscibility on the thermal stability of polymer blends [40–43], but, since the degradation product of a polymer can affect the stability of the other polymer even in immiscible blends, differences in stability between miscible and immiscible blends cannot be only explained in terms of miscibility. Moreover, some contrasting results have been reported [16].

The kinetic parameters for the thermal degradation were calculated using the Coats-Redfern equations [44]. For a reaction order, $n = 1$, the equation used is:

$$\log \frac{-\log(1-c)}{T^2} = \log \frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{2.3RT}$$

and for $n \neq 1$

$$\log \frac{1-(1-c)^{1-n}}{T^2(1-n)} = \log \frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{2.3RT}$$

where A represents the preexponential factor, β is the heating rate, and n is the apparent reaction order. A plot of the first member vs. $1/T$ gives a straight line from whose slope one can get the apparent activation energy, E_a. The conversion, c, is defined as:

$$c = \frac{w_0 - w_t}{w_0 - w_\infty}$$

where w_o and w_∞ are the initial and final weights and w_t is the weight at time t.

In Table II, the values of n and E_a for each degradation stage calculated in the temperature range indicated for all samples are shown. For all degradation steps, the value of n falls between 0.65 and 2.10. The activation energy found for the decomposition of DGEBA is 131.6 kJ/mol. The values of E_a given in the literature for epoxies usually refer to the cured resin [45, 46]. However, data for uncured DGEBA are scarce. For an

TABLE II Activation energies and reaction order calculated by the Coats-Redfern method for DGEBA/PVP blends

DGEBA/PVP	Stage in degradation	Temperature range (°C)	n	E_a (kJ/mol)
100/0	DER	182–302	0.65	131.6
90/10	DER	180–341	1.13	111.8
	PVP	341–471	1.58	214.7
80/20	DER	201–349	1.07	114.8
	PVP	349–454	1.28	213.3
70/30	DER	190–348	1.21	123.8
	PVP	348–460	1.33	248.4
60/40	DER 1	200–295	1.81	155.0
	DER 2	305–345	2.10	447.8
	PVP	350–460	1.36	264.8
50/50	DER 1	221–311	1.54	158.7
	DER 2	316–356	1.87	404.0
	PVP	361–462	1.23	269.4
40/60	DER 1	212–301	1.47	146.7
	DER 2	301–351	1.80	298.9
	PVP	356–467	1.32	258.7
30/70	DER	191–337	1.69	116.3
	PVP	352–472	1.12	231.3
20/80	DER	230–330	1.63	139.8
	PVP	365–460	1.25	284.5
10/90	DER	—	—	—
	PVP	354–458	1.35	299.8
0/100	PVP	366–471	1.28	292.1

uncured epoxy resin with the same chemical structure as the DGEBA used in this work but from a different supplier (Shell Epon 828), an activation energy of 128.3 kJ/mol was found [47]. This result, calculated both for isothermal and dynamic runs, agrees well with the value calculated here. For a phenoxy resin, which has a chemical structure similar to uncured DGEBA but of a much higher molecular weight, values of $E_a = 154.3$ kJ/mol calculated by the Kissinger method, and $E_a = 168.0$ kJ/mol determined by the Flynn-Wall method, have been reported [45]. It is known that different E_a values are usually obtained by different methods. These differences are generally ascribed to the different mathematical approaches used to evaluate the kinetic parameters [48]. In the case of the activation energy of phenoxy resin, the higher values obtained by Dyakonov *et al.* [45] as compared with our value for DGEBA, could be due, among other factors, to the different methods used for calculation as well as to the differences in molecular weight.

For PVP, unfortunately, no information concerning either the kinetic parameters or the mechanisms for thermal degradation has been reported in the literature during the last two decades. To our knowledge, only two papers have dealt with the thermal decomposition of PVP by TGA, but they only show the thermogravimetric curve of pure PVP and its blend with poly(*p*-hydroxystyrene) [49], and with polyamides [50]. The activation energy for the main degradation step of PVP calculated in this work by the Coats-Redfern method is 292.1 kJ/mol. With respect to the mechanism for the thermal degradation of PVP, this could not be established because the direct measurement of the thermal degradation products from the TGA apparatus requires extensive interfacing accessories that are not available in our laboratories at the present time.

Comparing the thermal stability of DGEBA and PVP, neglecting the very small low temperature degradation step of PVP, PVP has both a higher E_a and a higher temperature of maximum decomposition rate than DGEBA. Thus PVP is much more thermally stable than DGEBA.

The dependence of the activation energy of DGEBA/PVP blends on the PVP content is plotted in Fig. 5. All blends show two or three degradation stages. For the 10/90 sample, only the activation energy of the stage assigned to the main degradation of PVP has been calculated. The stage corresponding to the degradation of DGEBA appeared as a broad small shoulder, so that it was impossible to analyze by any of the current thermogravimetric analysis methods.

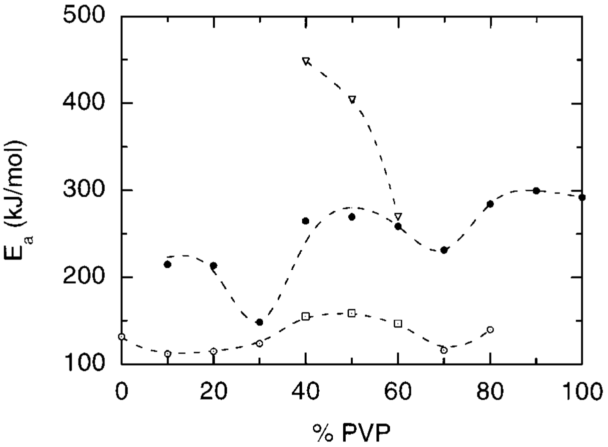

Figure 5 Activation energy vs. PVP content for the different degradation stages of DGEBA/PVP blends. ● PVP degradation stage, ○ DER degradation stage, □ DER 1 degradation stage, and ▽ DER 2 degradation stage.

As was seen in the DTG curves (Fig. 4), the blends containing 40, 50 and 60% of DGEBA presented two stages in the temperature range of degradation of DGEBA. The E_a values for these two stages are represented in Fig. 5 as open squares for the low temperature peaks, DER 1, and open triangles for the high temperature peaks, DER 2. A close examination of Fig. 5 reveals that the E_a calculated for the DER 1 stage is near to the E_a values obtained for the degradation step of DGEBA for the other blends (DER), whereas the E_a calculated for the DER 2 stage is surprisingly high, even higher than the E_a of pure PVP.

The E_a of the low temperature degradation stage of all blends, DER or DER 1, show two minima at the 90/10 and 30/70 compositions, and a maximum at the 50/50 blend. For the highest temperature degradation stage, named PVP, the calculated E_a also shows maxima and minima at roughly similar compositions.

To explain the results from Fig. 5 and Table II we have to take into account the different effects that are taking part concurrently in the process of degradation. Firstly, the viscosity of the environment, lower as the DGEBA content rises, influences the diffusion rate of the decomposition volatiles, so accelerating the weight loss. This effect could explain the destabilization of PVP mainly at high DGEBA contents.

Secondly, as is known [16], interactions are possible among the different species in the blend during degradation and among the products of degradation. These chemical reactions can lead either to an acceleration of the degradation rate with respect to that of the pure components or to a stabilizing effect. These reactions can be grouped into six processes:

- reactions between macromolecules and small molecules,
- reactions between macromolecules and small radicals,
- reactions between macroradicals and small molecules,
- reactions between two small molecules,
- reactions between two macroradicals,
- reactions between macromolecules and macroradicals.

Small molecules and radicals are products of the degradation of the pure polymers. These reactions give rise to new chemical species, which affect, not only the degradation behavior of the blend, but also other physical properties, for instance the viscosity. In addition, reactions with small molecules or small radicals can give rise both to faster breakage of the macromolecules and to chemical structures that act as stabilizer groups. Thus, the radicals produced during the degradation of PVP, a process which is initiated at about 200 °C, before the weight loss of pure DGEBA has started, could lower the production of free radicals in DGEBA to this temperature. Otherwise, as has already been mentioned, during the decomposition of DGEBA, radicals are also produced which can recombine with those coming from PVP yielding different kinds of copolymers with different compositions. Some of them, probably those richer in PVP, could cross-link attaining high molecular weights, so giving an increase in the E_a values. This would explain the high E_a values found in the 40/60, 50/50 and 60/40 blends for the DER 2 degradation stage. At these same compositions, the formation of other copolymers richer in DGEBA could also be possible. The E_a of these copolymers (DER 1 stage) would be near that encountered during the first degradation stage of the other blends (DER) and it seems to be reasonable to attribute this also to the degradation of copolymers rich in DGEBA formed at these compositions.

The effects influencing the thermal stability in DGEBA/PVP blends can, thus, be grouped into two types, those having a physical or a chemical origin. The contribution of both effects is not equal in E_a and in T_{max}. This could justify that those compositions more stable from the point of view of T_{max} are not exactly coincident with those considered more stable taking into account the E_a values.

4. Conclusions

Differential scanning calorimetry demonstrated the complete miscibility of DGEBA and PVP over the whole composition range. The glass transition temperature of this uncured system is reasonably well predicted by the Gordon-Taylor equation.

Thermogravimetry applied to the DGEBA/PVP blends permitted a degradation study. It was verified that DGEBA is more unstable than PVP under dynamic conditions in a nitrogen atmosphere. Both pure polymers decompose in a single stage, whereas their blends show a more complex degradation behavior, since they degrade in at least two stages. It is demonstrated that the stability of each polymer is influenced by the presence of the other component in the miscible blend. In this way, PVP exerces a stabilizing effect on DGEBA, producing a retardation of its decomposition manifested mainly by an increase in the temperature of maximum decomposition rate; but, at the same time, DGEBA destabilizes PVP, causing a decrease in its T_{max}.

The degradation of the blends appears to be governed by two effects, one physical and the other chemical in nature. The first varies monotonically with composition, but the second acts differently for each composition. The balance between these two effects is responsible for the maxima and minima observed in the activation energy. However, additional work would be necessary to gain a deeper knowledge of the thermal stability of this system.

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