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Study of poly(ethylene oxide)/Carbopol blends through thermal analysis and infrared spectroscopy

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Abstract

Properties such as miscibillity, interaction and the thermal degradation behavior of blends of poly(ethylene oxide) (PEO) with Carbopol were studied by thermal analysis (DSC, TGA) and infrared spectroscopy (FTIR). The miscibility of PEO/Carbopol blends in all composition ranges was confirmed, and the interaction is favored by hydrogen bonding between the carboxylic acid group of Carbopol and the PEO ether oxygen. TGA analysis showed that, with temperature increase, anhydride formation occurred first, confirmed by the FTIR bands in 1806, 1756 and 1047 cm^{-1}. Thermal degradation products such as carbon dioxide appear as a result of fragmentation of the anhydride ring structures and decarboxylation of the Carbopol acid groups. Bands related with unsaturated structures (1605 cm^{-1}) were observed at 310°C and 470°C, presumably as a result of scissions of the main carbon–carbon chain. The activation energy of PEO/Carbopol blends increased with the Carbopol content in the blend, indicating that the thermal degradation is delayed with the presence of Carbopol. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Miscibility; Hydrogen bonding; Thermal degradation

1. Introduction

Poly(ethylene oxide) (PEO) is one of the most extensively studied water soluble polymers in the last decades, and, in general, has been used as a component of innumerable polymer blends with the purpose of analyzing properties such as miscibility, crystallization processes, and interaction parameters. For example, blends of PEO with poly(methyl methacrylate) (PMMA) [1–3] or poly(vinylacetate) (PVAc) [4–6], show clear evidence of miscibility (or partial miscibility) in the melt state of PEO with both polymers. The addition of poly(ethyl methacrylate) (PEMA) to PEO affects the crystallization process from the melt and the melting temperature of PEO [7]. Studies of all the above systems, using different techniques, have indicated that the polymers are miscible with the amorphous phase of PEO.

Another important system is formed by the mixture of PEO and poly(acrylic acid) (PAA), mainly because PAA is used as an agent in lattices and adhesives and also in the formulation of pharmaceutical products, cosmetics and agricultural chemicals [8,9]. The interaction between PEO and PAA, in general, is favored by hydrogen bonding between the components, forming an insoluble complex in water [8–11]. The complex formation depends on temperature, pH, polymer concentration, solvent and hydrophobic interactions [12]. Studies have shown that this interaction is estoichiometric, independent of the molecular weight of PEO [10]. Solid mixtures of PEO and PAA, obtained after solvent evaporation, are miscible at all composition ranges and the newly-formed material shows a high flexibility in contrast to the pure components. Studies on PEO/PAA blends properties have been related with low molecular weight PAA, and details about the hydrogen bonding, crystallization and mechanical properties of the new material are open to specific investigation.

The purpose of this work was to analyze the interaction of PEO with a high molecular weight Carbopol which have a small degree of cross-linking in their structure. Details about miscibility and hydrogen-bonding interactions are also reported. Other aspects discussed include the thermal stability of the formed complex, mainly with relation to the activation energy and mechanism of the thermal degradation reaction.

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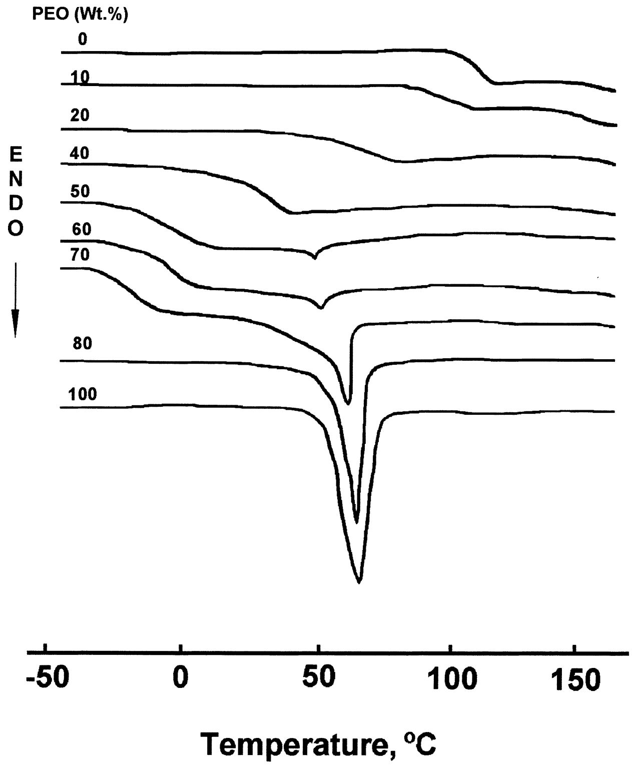

Fig. 1. DSC thermograms of pure components and PEO/Carbopol blends with different percentages of PEO, as indicated, at a heating rate of 10 °C min^{-1}.

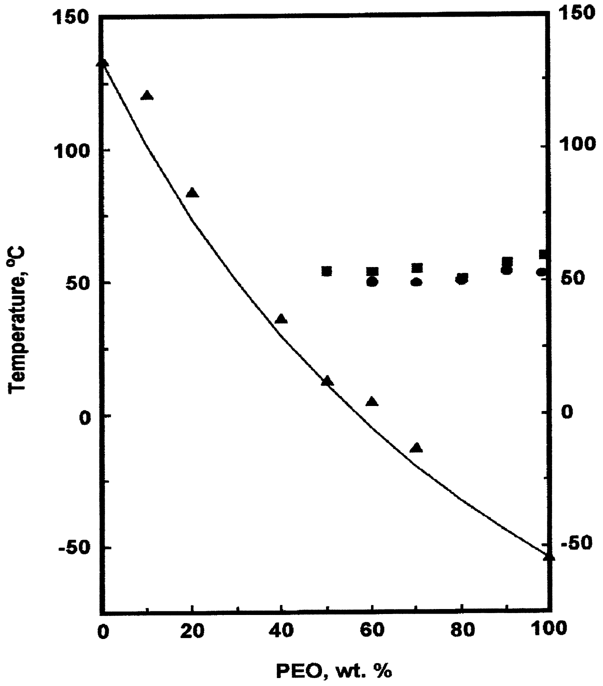

Fig. 2. Transition temperatures as a function of PEO in PEO/Carbopol blends: (▲) T_g; (■) T_m and (●) T_c. The solid line represents the values obtained from Eq. 1.

2. Experimental section

2.1. Materials

PEO with a nominal molecular weight of 300 000 g mol^{-1} was received from Aldrich. Carbopol-934P, with a carboxylic acid content of 56 to 68% and molecular weight higher than 3 000 000 g mol^{-1}, was kindly supplied by BF Goodrich. Both polymers were used without further purification. Deionized water was used in all sample preparation.

2.2. Sample preparation

The pure polymers were dissolved in water by stirring at room temperature for at least 12 h. PEO/Carbopol blends were prepared by mixing different amounts of the components to obtain blends with different compositions. The homogeneous solutions were left at room temperature until the solvent had evaporated. The blend-films were then dried in a vacuum at 40°C before use.

2.3. Techniques

DSC thermograms were obtained on a Shimadzu 50 differential scanning calorimeter by heating from −100 to 200°C at 10 °C min^{-1}. For all measurements, the samples were heated and maintained for 10 min at 200°C and then slowly cooled, after which a second scan was performed and used for the transition values. The average sample size was 5 mg and the nitrogen flow-rate was 25 cm^3 min^{-1}.

Thermogravimetric measurements were carried out on a Shimadzu 50 thermogravimetric analyzer. Non-isothermal experiments were performed in the temperature range 25 to 500°C at heating rates of 5, 10 and 20 °C min^{-1} on each sample. The average sample size was 5 mg and the nitrogen flow-rate was 25 cm^3 min^{-1}. The thermogravimetric data were analyzed using the Osawa method [13–15] and the parameters determined using the associated TGA-50 software. The activation energy was derived from the slope of the dependence of the heating-rate upon the reciprocal absolute temperature, at defined mass loss.

Infrared spectrocopy (FTIR) was performed on Perkin Elmer equipment (model 16PC) using sample films prepared on ZnS plates.

3. Results and discussion

3.1. Differential scanning calorimetry

Fig. 1 shows the DSC thermograms for the undiluted components and PEO/Carbopol blends. Crystallization (T_c) (not shown in Fig. 1) and melting temperatures (T_m) of undiluted PEO were 53 and 62°C, respectively. The PEO glass transition temperature (T_g) was unobtainable under this condition, by DSC. However, pure Carbopol

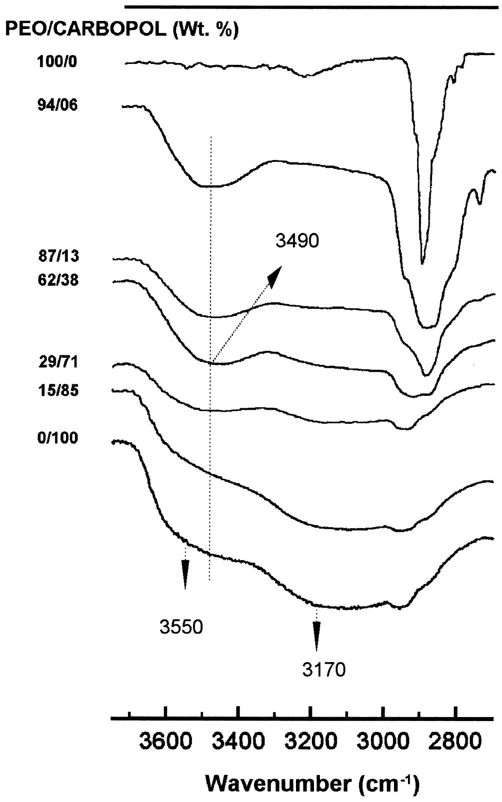

Fig. 3. FTIR spectra for pure components and PEO/Carbopol blends in the region of 3700 to 2700 cm^{-1}.

gave a T_g of 133°C. The T_g of Carbopol changed to lower values with the increase of the PEO composition, suggesting miscibility. On the other hand, a slight increase in the PEO melting temperature was observed.

Fig. 2 shows the dependence of the transition temperatures for pure components and PEO/Carbopol blends, obtained through the DSC thermograms, as a function of the PEO composition. The T_g of the amorphous components decreases monotonically with the increase of the semi-crystalline component composition in the blend. Slight increases in T_c and T_m values of PEO were observed. In Fig. 2, the solid line represents the T_g values determined through the Fox equation (Eq. 1), where T_{gb} is the blend glass transition temperature, w_1 and w_2 are the PEO and Carbopol weights in the blend respectively, and

$$\left[\frac{1}{T_{gb}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}\right] \qquad (1)$$

T_{g1} and T_{g2} are the glass transition temperatures for the undiluted components. The theoretical (determined by the Fox equation) and experimental values shown in Fig. 2 coincide, suggesting miscibility between the components in all composition ranges, as observed for similar systems reported in the literature [10,11,16,17].

3.2. Infrared spectroscopy

If two polymers are miscible, the FTIR spectra show considerable difference in comparison with the undiluted components. Essentially, the interactions can shift or change the band intensities and broaden the corresponding vibrations of the pure components [16,18–20].

The interaction of the PEO ether oxygen with the carboxylic acid group of the Carbopol can be analyzed by FTIR in order to obtain information about intermolecular hydrogen bonding between the components of the blend. For example, Colemam et al. [21], using FTIR spectroscopy, reported changes in the carbonyl stretching of poly (caprolactone) with the addition of poly(vinyl chloride), due to the favored hydrogen bonding between the components. In the same way, hydrogen bonding is also responsible for the miscibility between PMMA and styrene–acrylic acid copolymer [22]. Xinya Lu and R.A. Weiss [11] studied the interaction by hydrogen bonding between the ether group of poly(glycol ethylene) and the carboxylic group of the partially neutralized poly acrylic acid, where the carbonyl band of the acid was 1706 cm^{-1} and the free hydroxyl bands formed intramolecular hydrogen bonding at the range of 3000 to 3600 cm^{-1}. It is known in general that poly acrylic acids show typical intermolecular hydrogen bonds at ca. 3170 cm^{-1} (bonded) and at ca. 3550 cm^{-1} (free hydroxyl) [8,9].

The FTIR spectra of pure components and different compositions of PEO/Carbopol blends in the 4000 to 2700 cm^{-1} region are shown in Fig. 3. In the Carbopol spectra, we may observe a broad and intense band corresponding to the overlap of two bands at ca. 3550 and ca. 3170 cm^{-1}, related to the free hydroxyl group and the hydroxyl-forming intramolecular hydrogen bonding, respectively. It is quite clear that with the PEO percentage increased, the band at ca. 3170 cm^{-1} decreases in intensity and the band at ca. 3550 cm^{-1} shifts to a lower vibration. The decrease of the band at ca. 3170cm^{-1}, corresponding to the Carbopol intramolecular hydrogen bonding, is not only caused by the PEO/Carbopol interaction but also by the decrease in the acid-group concentration. The shift of the band corresponding to the free hydroxyl groups from ca. 3550 cm^{-1} to ca. 3490 cm^{-1} indicates that, with the PEO/Carbopol interaction, the OH···O–C hydrogen bonding is formed. In PEO-rich blends, the OH···O–C interaction predominates, although a small amount of free hydroxyl groups may still be present. The small shift (ca. 60 cm^{-1}) in the hydroxyl stretching vibration indicates a weak hydrogen bonding interaction caused by the lower oxygen electron availability of the PEO ether group in comparison with the oxygen carbonyl of Carbopol. Similar results were observed for the PMMA/Poly(4-vinyl phenol) (PVPh) interaction, in which a band at 3540 cm^{-1}, corresponding to the phenol free hydroxyl groups, shifts to 3350 cm^{-1} when the OH···O=C interaction with the PMMA carbonyl group occurs [9]. In this case, the shift of ca. 200 cm^{-1} indicates

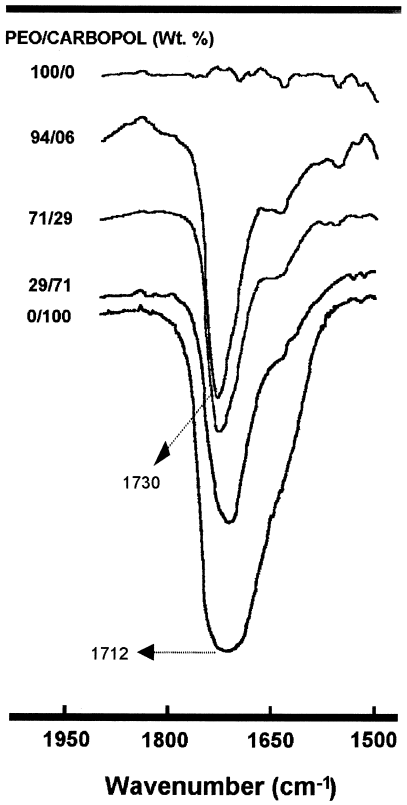

Fig. 4. FTIR spectra for pure components and PEO/Carbopol blends in the region of 1950 to 1500 cm^{-1}.

a stronger interaction compared with the system studied in this work.

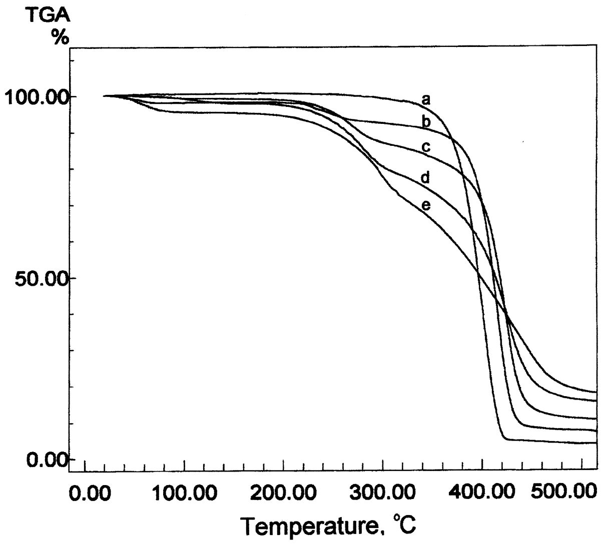

Fig. 5. Thermogravimetric curves of pure components: (a) PEO; (e) Carbopol and PEO/Carbopol blends: (b) 80/20; (c) 50/50 and (d) 20/80. All the represented thermogravimetric curves were performed at a heating rate of 5 °C min^{-1} in nitrogen.

Table 1
Thermogravimetric and kinetic parameters to pure components and PEO/Carbopol blends

PEO/Carbopol[a] (°C)	T_{MAX}[b] (kJ mol^{-1})	E_a[c]	Log Z (%)	Residual[d]
100/0	402	151.7	11.1	4
80/20(A)	240	57.9	7.5	
80/20(B)	413	152.2	12.2	8
50/50(A)	272	111.4	8.2	
50/50(B)	422	179.2	12.9	10
20/80(A)	274	94.0	7.4	
20/80(B)	422	172.5	12.2	11
0/100(A)	296	107.0	8.5	
0/100(B)	434	224.0	15.4	20

[a] In the blends compositions and pure carbopol, (A) and (B) represent the first and second stages, respectively, of thermal degradation discussed in the present work.

[b] Determined considering the TGA derivative.

[c] Determined as the average of the values plotted in Fig. 6.

[d] Values determined at 550°C in a heating rate of 5 °C min^{-1}.

In the region of 1950 to 1500 cm^{-1} (Fig. 4), the Carbopol shows an intense and broad band (1712 cm^{-1}) corresponding to the carbonyl stretching. The broadening of the carbonyl stretching band of pure Carbopol is attributed to the presence of two carbonyl populations, one corresponding to the intra- and intermolecular hydrogen bonding (OH···O=C) and another due to a free carbonyl group. This band tends to change to a higher vibration frequency with the increase of the PEO composition, indicating changes of acid–acid intramolecular hydrogen bonding of Carbopol by the acid–ether bonding of the PEO/Carbopol blend. As a consequence, the increase in the number of free carbonyl groups of Carbopol results in an intense band observed at 1730 cm^{-1} in blends with more than 71% of PEO. Similar behavior was observed by Kim et al. [23] for PHMP/PMMA blends and by Akiba et al. [24] for PEG/P(S-co-MAA).[1]

The above results show that the interactions in the PEO/Carbopol blends are due to the hydrogen bonding between the Carbopol hydroxyl group and the ether oxygen of the PEO.

3.3. Thermal degradation

The thermal degradation was studied in order to evaluate the thermal stability and kinetic parameters as activation energy. Fig. 5 represents the relationship of the residual weight fraction to temperature for pure components and PEO/Carbopol blends at a heating rate of 5 °C min^{-1} under a nitrogen atmosphere. For pure Carbopol and blends, the TGA thermograms clearly show that more than one process occurred during thermal degradation. Pure Carbopol (curve e), for example, shows three stages of thermal degradation until approximately 550°C. However, in the same temperature range, the PEO (curve a) shows just one stage, leading to almost 100% mass loss. The residual

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[1] P(S-co-MAA): poly(styrene-co-methacrylic acid).

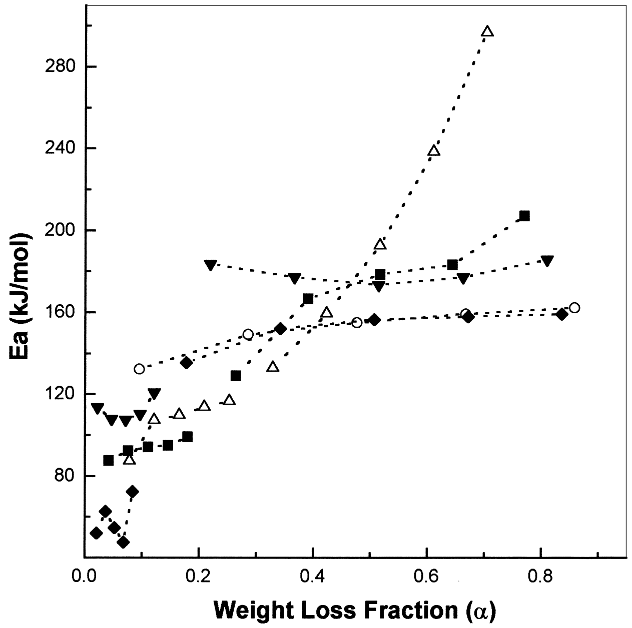

Fig. 6. Plots of activation energy versus weight-loss fraction for pure components ((○) PEO and (△) Carbopol) and PEO/Carbopol blends ((◆) 80/20; (▼) 50/50 and (■) 20/80).

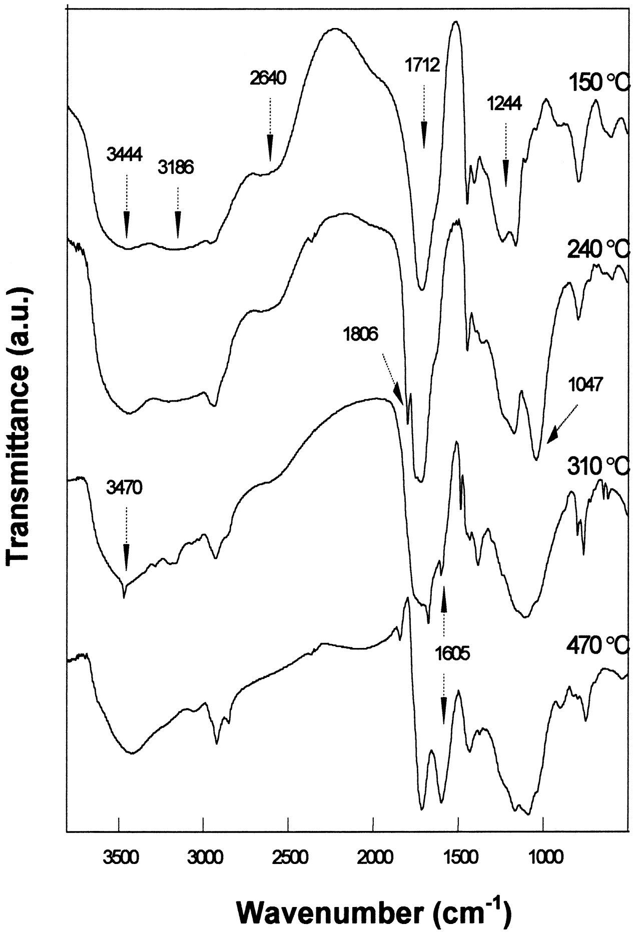

Fig. 7. FTIR spectra of pure Carbopol during thermal degradation at different temperatures.

weight percentage at 550°C increases with the Carbopol content in the blend, rising to approximately 20% in pure Carbopol (Table 1).

For the kinetic studies, we considered only the two major processes of degradation as indicated for the maximum temperatures in Table 1 (processes A and B). The activation energy of pure components and blends determined using the Ozawa method [13–15] versus the weight loss fraction (α) are shown in Fig. 6. For pure Carbopol, the activation energy increases with the increase in weight-loss fraction, rising to approximately 300 kJ mol^{-1} when $\alpha = 0.7$. The activation energy varies with conversion, and is probably related with changes in the mechanism of degradation. On the other hand, both assumptions must be related with the occurrence of more than one stage of degradation in the system. Therefore, in relation to pure PEO, the values remain practically the same (average value of 151.7 kJ mol^{-1}) in the weight-fraction range of 0.3 to 0.85. This behavior agrees with the occurrence of just one degradation stage in pure PEO. Blends with 80% PEO gave very low activation energy values in the first stage of degradation (A) and similar values of pure PEO in the second stage (B). With increasing Carbopol content in the blend, the activation energy values also increase in both stages of degradation. The average values for the second stage, shown in Table 1, increase with the Carbopol content in the blend. In general, this effect indicates that thermal degradation is delayed by the addition of Carbopol. Similar behaviour was reported by Chiu et al. [25] for blends of poly(methyl methacrylate) and propyl ester phosphazene and by Chan and Balke [26] for the thermal degradation of polypropylene. The pre-exponential factor *Z*, on the other hand, shown for the PEO/Carbopol blends (Table 1), has very similar values in the first stage of degradation (A) and values related to the activation energy in the second stage (B). For pure PEO, the pre-exponential factor is proportional to the activation energy value, like the second degradation stage in the blend.

The mechanism of degradation was evaluated through FTIR spectra at different temperatures during thermal treatment. As Carbopol showed more than one degradation stage, we analyzed the FTIR spectra at different degradation temperatures of pure Carbopol (Fig. 7), and PEO/Carbopol blends with 50% PEO composition (Fig. 8).

As discussed earlier (see the infrared spectroscopy discussion), the undergraded Carbopol shown in the region between 3100 and 3550 cm^{-1}, typical bands of hydroxyl stretching (Fig. 3). For Carbopol, broad peaks with a maximum above 3400 cm^{-1} correspond to hydroxyl-free groups related to carboxylic groups. In general, these bands shift up to ca. 3550 cm^{-1}, depending on the degree of free hydroxyl groups. The band at ca. 3170 cm^{-1} corresponds to the hydroxyl groups, forming intramolecular hydrogen bonding. The carbonyl stretching band caused by carboxylic groups is evident at ca. 1712 cm^{-1} (Fig. 4). Other relevant

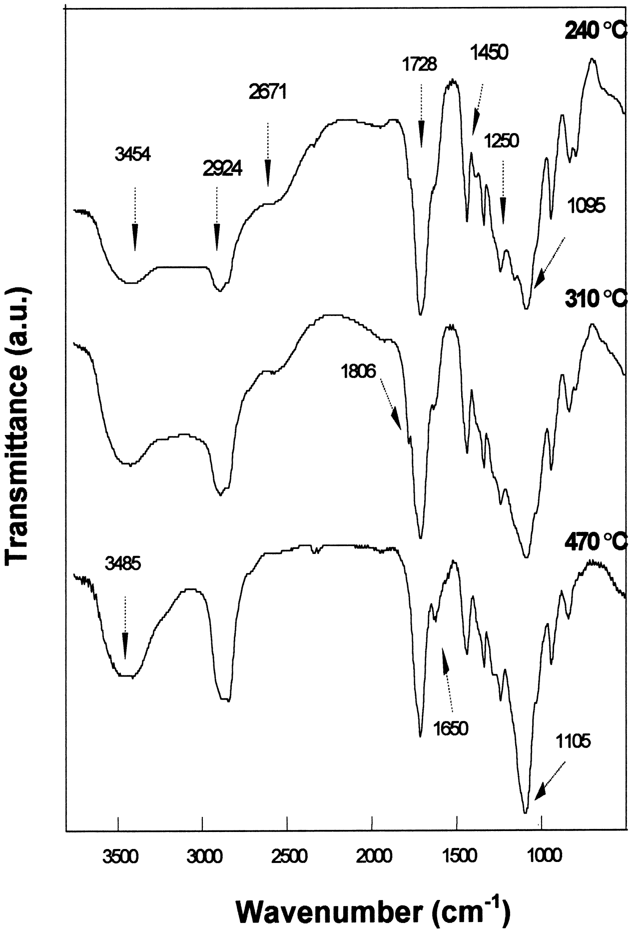

Fig. 8. FTIR spectra of PEO/Carbopol (50/50) blends during thermal degradation at different temperatures.

bands (not shown in Fig. 4) are associated with CH_2 and CH_3 out of plane (1455 cm^{-1}) and with the carbonyl or hydroxyl groups (1244 and 1167 cm^{-1}).

The FTIR spectra of pure Carbopol at different degradation temperatures, corresponding to treatment up to 150, 240, 310 and 470°C, are shown in Fig. 7. After treatment up to 150°C, the spectra seem very similar to those of the undergraded Carbopol, therefore, all the bands are shifted to higher values. These spectra correspond to a weight loss of ca. 5%, and the band-shifts observed are probably related to the decrease in the associated water–carboxylic groups caused by the water loss in this system (not discussed in this work). In general, the shift of the free-hydroxyl-groups band (3433 cm^{-1}) to higher values, indicates that more free carboxylic groups are present. At 240°C, the spectra corresponding to a weight loss of ca. 30% show the appearance of absorptions at 1806, 1756 and 1047 cm^{-1}, in general associated with a formation of cyclic structures. In this system, similar to other systems described in the literature [27,28], an anhydride formation occurs which is confirmed by the C–O–C stretching vibrations at 1047 cm^{-1}. Apparently, the anhydride appears as an intermediate structure, disappearing at 310°C. At this temperature, the shift of the band from 3440 to 3470 cm^{-1} indicates that more isolated carboxylic groups are present. At the same temperature, a new band at ca. 1605 cm^{-1} related to the unsaturated structures also appears. This band increases in intensity at 470°C, indicating an almost complete degradation. The identification of CO_2 among the products (at ca. 2360 cm^{-1}) indicates the Carbopol acid groups decarboxylation. In blends with 50% Carbopol (Fig. 8), a similar behavior was observed at all the degradation temperatures analyzed. The bands show some shifts and lowering of intensities in comparison with pure Carbopol, but the presence of the bands corresponding to anhydride formation, unsaturated structures and products discussed above is very clear.

4. Conclusions

The thermal analysis results confirm the miscibility of PEO/Carbopol blends in all composition ranges. The interaction is favored by hydrogen bonding between the carboxylic acid group of Carbopol and the PEO ether oxygen, as was shown through FTIR. For Carbopol and blends, the TGA thermograms clearly show that more than one process occurred during thermal degradation. However, with pure PEO just one degradation stage is observed. The activation energy increases with the Carbopol composition in the blend, clearly showing that the thermal degradation is delayed with the presence of Carbopol. With the temperature increase, anhydride formation (as an unstable intermediate) occurs first, and this in turn is degraded, forming carbon dioxide and other radicals as products. The complete degradation also includes the decarboxylation of the Carbopol acid groups. The observed bands related with unsaturated structures are indicative of scission of the main carbon–carbon chain.

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References

[1] Martuscelli E, Pracella M, Yue WP. Polymer 1984;25:1097.
[2] Straka J, Schmidt P, Dybal J, Schneider B, Spevacek J. Polymer 1995;36:1147.
[3] Imai S, Shimono S, Fukushima Y, Umezaki K, Okada M, Takahashi M, Matsuda H. Thermochim Acta 1995;267:259.
[4] Han CD, Chung HS, Kim JK. Polymer 1992;33:546.
[5] Yin J, Alfonso GC, Turturro A, Pedemonte E. Polymer 1993;34:1465.
[6] Wu WB, Chiu WY, Liau WB. J Appl Polym Sci 1997;64:411.
[7] Cimmino S, Martuscelli E, Silvestre C, Canetti M, De Lalla C, Seves A. J Polym Sci Polym Phys Ed 1989;27:1781.
[8] Dong J, Ozaki Y, Nakashima K. Macromolecules 1997;30:1111.
[9] Dong J, Ozaki Y. Macromolecules 1997;30:286.

[10] Jeon SH, Ree T. J Polym Sci Polym Chem Ed 1988;26:1419.
[11] Xinya Lu, Weiss RA. Macromolecules 1995;28:3022.
[12] Tsuchida E, Abe K. Adv Polym Sci 1982;45:1.
[13] Ozawa T. Bull Chem Soc Japan 1965;38:1965.
[14] Ozawa TJ. Thermal Anal 1970;2:301.
[15] Ozawa TJ. Thermal Anal 1975;7:601.
[16] Chu CH, Berner B. J Appl Polym Sci 1993;47:1083.
[17] Aubin M, Voyer R, Prud'homme RE. Makromol Chem Rapid Comm 1984;5:419.
[18] Sotele JJ, Soldi V, Pires ATN. Polymer 1997;38:1179.
[19] Iriondo P, Iruin JJ, Berridi MJF. Macromolecules 1996;29:5606.
[20] Dong J, Ozaki Y. Macromolecules 1997;30:286.
[21] Coleman MM, Zarain I. J Polym Sci Polym Phys Ed 1979;17:837.
[22] Jo WH, Cruz CA, Paul DR. J Polym Sci 1989;27:1057.
[23] Kim H-Il, Pearce EM, Kwei TK. Macromolecules 1989;22:3374.
[24] Akiba I, Ohba Y, Akiyama S. Macromolecules 1999;32:1175.
[25] Denq B, Hu Y, Chiu W, Chen L, Chiu Y. Polym Degrad Stab 1997;57:269.
[26] Chan JH, Balke ST. Polym Degrad Stab 1997;57:135.
[27] Zulfigar S, Masud K, Piracha A, McNeill IC. Polym Degrad Stab 1997;55:257.
[28] Lazzari M, Kitayama T, Hatada K, Chiantore O. Macromolecules 1998;31:8075.