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Poly(vinyl alcohol) and poly(vinylpyrrolidone) blends: 2. Study of relaxations by dynamic mechanical analysis

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Abstract

Blends of poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) were studied by dynamic-mechanical analysis (DMA). PVA with different degrees of hydrolysis (88 and 99 wt%) and PVP with different molecular weights (10.000 and 360.000 g/mol) were used to prepare the blends. DMA results showed that blends were miscible over the whole composition range studied. However, the E'' modulus curves exhibit relaxations at the same temperature range below Tg for all blends, suggesting the presence of microenvironments in the blends. These microenvironments are associated to the hydrogen bonding between PVA–PVA in the crystalline and amorphous phase and PVP–PVA in the amorphous phase and in the amorphous–crystalline interface. The stiffness and the flexibility of these blends at 200°C depend strongly on the blends composition, the molecular weight of PVP and the hydrolysis degree of the PVA as determined by the E' modulus curves. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Over the last decades the miscibility of blends of poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) has been intensively investigated. Eguiazábal et al. [1] reported the miscibility of the blends only for PVA with a hydrolysis degree higher than 70 wt%. Nishio et al. [2] observed only a glass transition for the blends of 99.7 wt% hydrolysed PVA and PVP. The polymer–polymer interaction parameter was determined using the melting point depression method, yielding a negative value independent of the composition. Similar results were described by Ping et al. [3]. In ^{13}C-NMR solid state studies, Feng et al. [4] and Zang et al. [5], demonstrated the miscibility in this system and the existence of the H-bonding between the polymers.

Ping et al. [4] studied PVA/PVP blends by infrared spectroscopy and they found that this system contains organized regions, which were attributed to the hydrogen bonding between PVA–PVA and PVA–PVP chains. In our previous work [6] we related the heat capacity change and the glass transition width dependence on the blends composition, the hydrolysis degree of PVA and molecular weight of PVP and the results were explained based on Ping's model.

Organized regions or microenvironments exhibit different compositions and density of hydrogen bonding interactions, which is defined as the number of interactions between PVA and PVP chains per volume of sample. The different microenvironments present relaxations occurring in characteristic relaxation times, which are related to the glass transition or secondary relaxations. Secondary relaxations involve rotational and vibrational motions of the side groups of the chains or small segments of the chain [7]. Low energy and low heat capacity changes are associated with these relaxations that occur at temperatures below Tg. As a consequence of these characteristics, sensitive techniques must be used for this aim, such as NMR, dynamic mechanical analysis (DMA), dynamic dielectric analysis (DEA), etc.

In the present work we studied the secondary relaxations of the PVA/PVP blends by DMA. The temperature and the intensity of relaxations were evaluated as functions of the blends composition and the hydrolysis degree of PVA.

2. Experimental

2.1. Polymer materials

In Table 1 the properties of the polymers used to prepare the blends are summarized.

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Table 1
Polymers used in this study

Code	Degree of hydrolysis (%)	Mw (g/mol)	Source
PVA 99	99	124.000	Aldrich
PVA 88	87,7	127.000	Rhodia
PVP 10	–	10.000	Sigma
PVP 360	–	360.000	Sigma

2.2. Cast films

Blends with different compositions were prepared in the same way as described in our previous work [6].

2.3. Dynamic-mechanical analysis

The dynamic-mechanical analysis (DMA) of the blends was carried out by means of a DMA 983 (DuPont Instruments), at a frequency of 1 Hz from −50 to 200°C. Samples of dimension ca. 1.00 × 0.26 × 0.12 cm were submitted to sinusoidal deformation with 0.20 mm of amplitude. The samples were heated in steps of 3°C, remaining at each temperature for enough time to reach thermal equilibrium.

3. Results and discussion

3.1. Loss modulus behavior

The curves of loss modulus as a function of the temperature (E'' *x* T) for the homopolymers, PVA 99, PVA 88 and PVP 360, and their blends are shown in Fig. 1. Each curve was shifted in relation to the other to facilitate the presentation of the results.

The temperature corresponding to the maximum of the peaks or shoulders in the E'' *x* T curves are assumed to be the relaxation temperature: glass transition (Tg) or secondary relaxation (Ts). The Tg and Ts for PVA99/PVP 360 blends are shown in Table 2.

PVA 99, Fig. 1(a), presents an intense relaxation with maximum at 86°C attributed to the glass transition and a shoulder at 50°C associated with the local molecular motions or conformational changes of the PVA side groups [7]. PVP 360 presents a broad relaxation at 100°C (Ts_c), attributed to the free-volume fluctuations and a relaxation at 187°C related to the glass transition relaxation [7].

In PVA 99/PVP 360 blends two secondary relaxations can be observed at 50°C (Ts_a) and at 85°C (Ts_b) (Fig. 1(a)). The relaxation intensities show a blend composition dependence on the rise of PVP concentration, which leads to an inversion in the intensity of the relaxations at 50°C and at 85°C. The relaxation at 50°C, which appears as a shoulder in

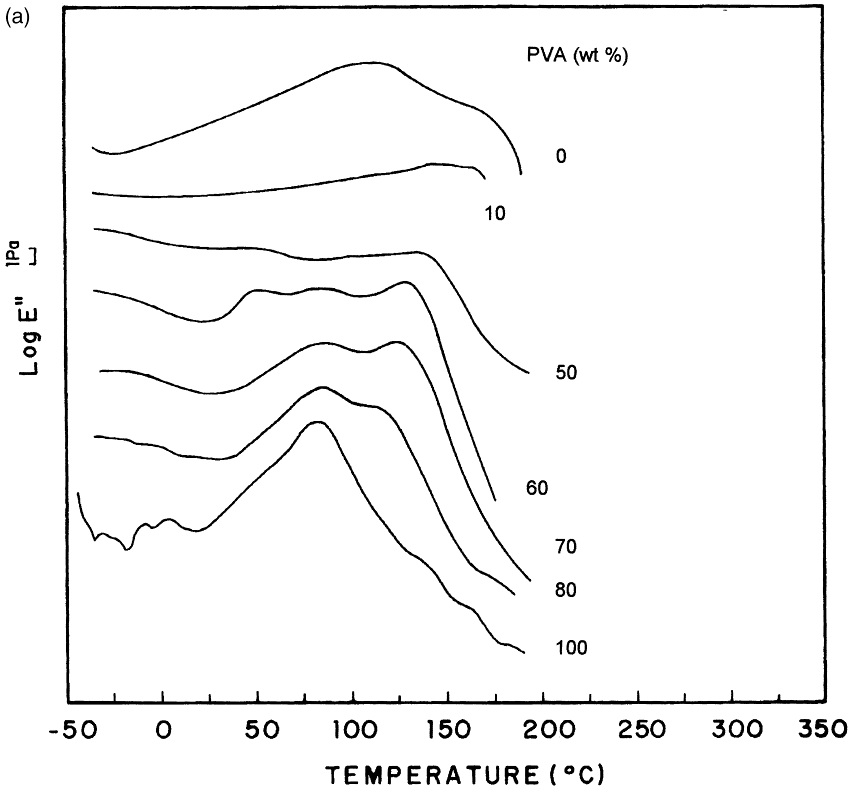

Fig. 1. Curves of loss modulus (E'') as a function of the temperature for the blends: (a) PVA 99/PVP 360 and (b) PVA 88/PVP 360.

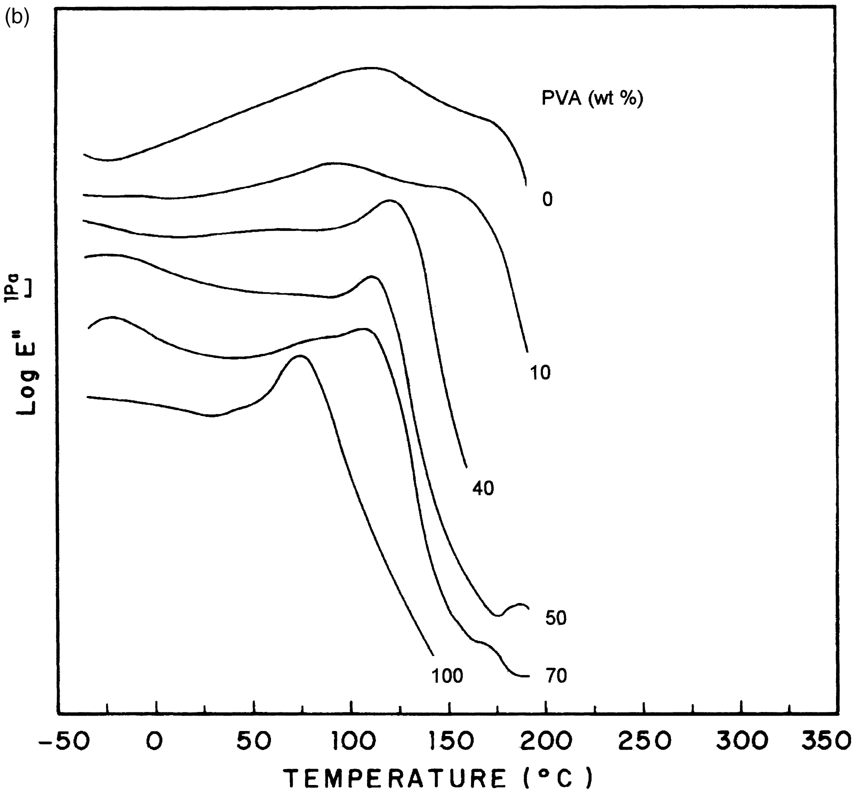

Fig. 1. (*continued*)

blends with 20 and 30 wt% of PVP becomes a broad but defined peak at the same temperature range for blends containing higher PVP concentration. On the other hand, the defined relaxation at 85°C in lower PVP concentration, becomes a shoulder according to the rise of PVP concentration, and vanished at higher PVP content. However, the temperature range where these relaxations occur does not depend on the blends composition. The transition at 85°C could be related to the glass transition of the PVA, and in this case the blend must be heterogeneous. But the DSC curves [6] showed only a very defined glass transition for all blends composition, and the polymer–polymer interaction parameter was negative. Therefore, there is no evidence for phase segregation, and the relaxation is attributed to the microenvironments or to the microregions present in the composition of all blends. These microenvironments are associated with the local hydrogen bond formation between PVA–PVA and PVP–PVA, as proposed by Ping's model [4].

The relaxation process at 50°C is more evident in blends rich in PVP, i.e., in blends exhibiting lower or no crystallinity. Therefore, it is attributed to the reorganization of the hydrogen bonding in the amorphous region. The secondary relaxation at 85°C can be related to the relaxations of the chain segments involved in hydrogen bonding interactions in the crystalline–amorphous interphase, since this relaxation can only be observed in blends which exhibit a crystalline phase, as detected by DSC [6]. The chain segments near the crystalline phase are more rigid and therefore a higher energy is necessary to promote conformation changes.

Table 2
Glass transition temperature (Tg) and secondary relaxation temperature (Ts) for the blends PVA 99/PVP 360

PVA (wt%)	Ts_a [a](°C)	Ts_b [a] (°C)	Ts_c [a] (°C)	Tg (°C)
100	56	–	–	83
90	50	84	–	114
50	50	86	–	125
40	49	86	–	129
30	55	85	–	138
40	–	–	100	174
0	–	–	109	184

[a] Ts_a and Ts_b: PVA secondary relaxations; Ts_c: PVP secondary relaxation.

Table 3
Glass transition temperature (Tg) and secondary relaxation temperature (Ts) for the blends PVA 88/PVP 360

PVA (wt%)	Ts (°C)	Tg (°C)
100	45	75
90	45–107	107
60	45–114	114
50	45–121	121
30	45–179	179
0	45–184	184

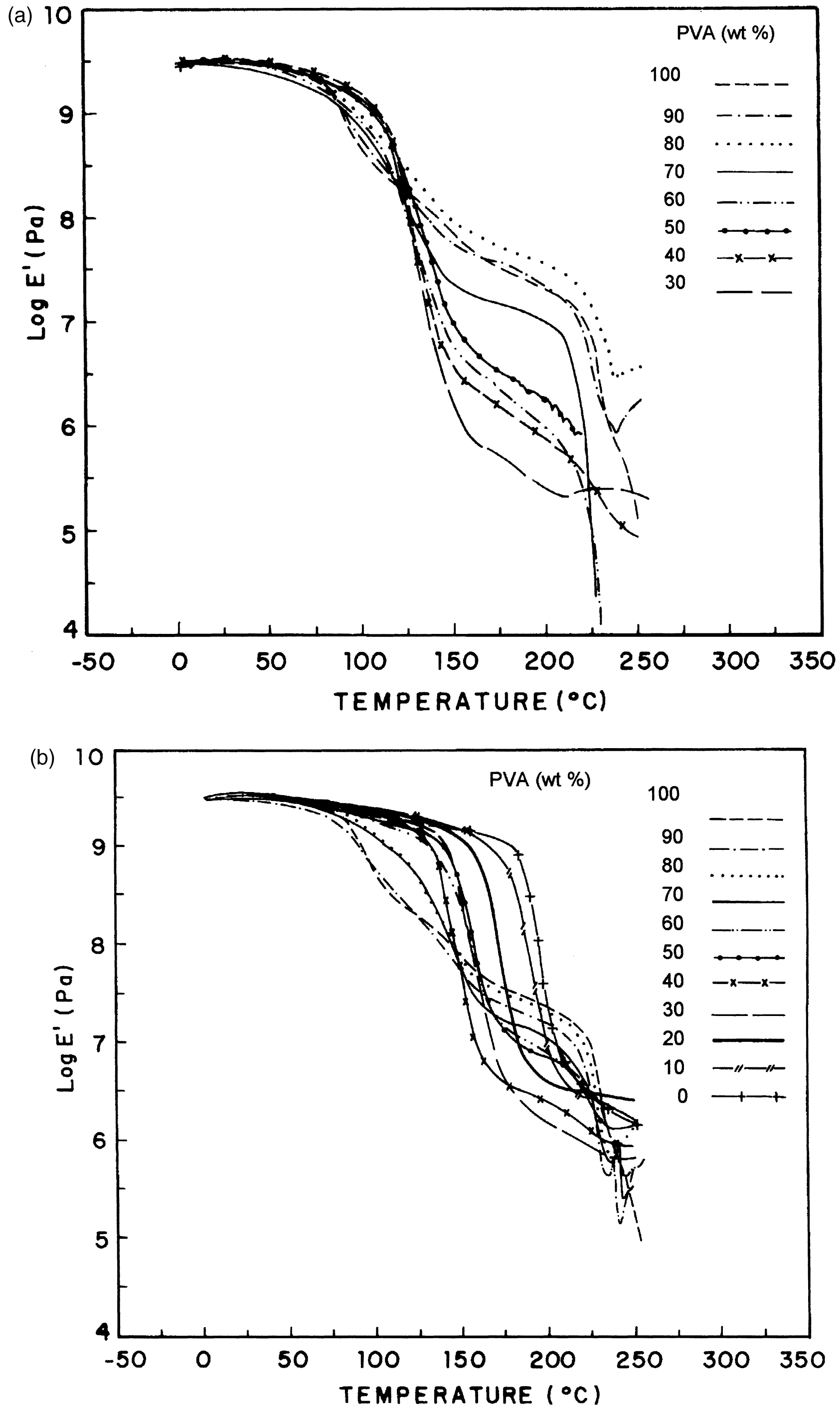

Fig. 2. E′ modulus versus temperature curves obtained for the blends: (a) PVA 99/PVP 10, (b) PVA 99/PVP 360, (c) PVA 88/PVP 10 and (d) PVA 88/PVP 360.

PVA 99/PVP 360 blend containing 40 wt% of PVP showed close intensity values for the two secondary relaxation processes. This fact indicates that in this concentration there should be a larger density of interactions in the different microenvironments in this system, which agrees with the data of our previous work [6], where the glass transition in PVA 99/PVP 360 blends is broader at PVP concentrations of 40 and 50 wt%.

The behaviour of the E″ curves for blends containing PVA 88 is similar to that observed for the blends of PVA 99 (Fig. 1(b) and Table 3). PVA 88 presented a shoulder at 46°C, related to the secondary relaxation, and a relaxation at a higher temperature, 83°C, which was attributed to the glass transition. In PVA 88/PVP 360 blends only one secondary relaxation process was observed as can be seen in Fig. 1(b), which occurs from 45°C to the Tg. This broad

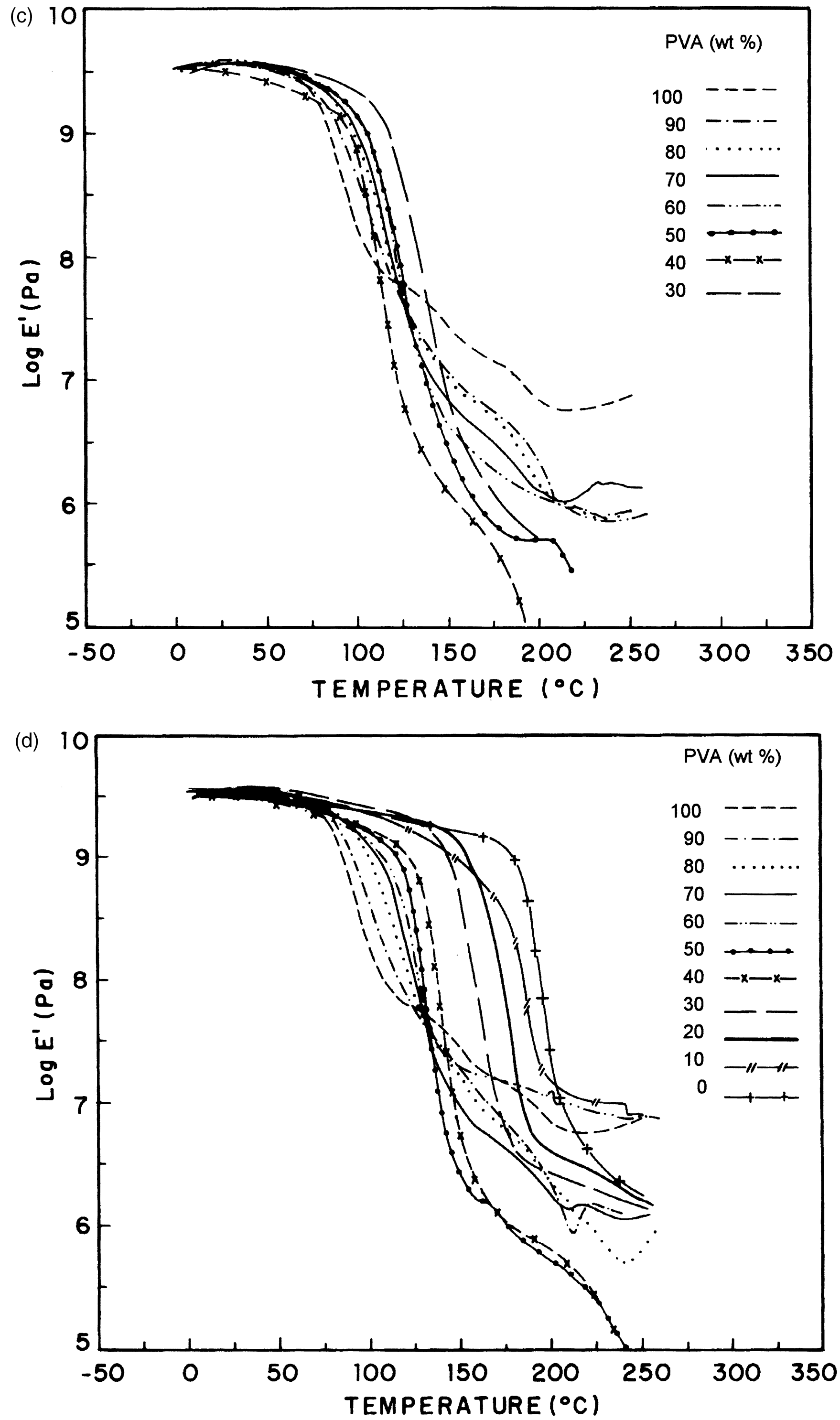

Fig. 2. (*continued*)

relaxation can be due to the overlap of relaxations of amorphous and amorphous–crystalline interface regions in the blends and to the secondary relaxation associated with the PVP. This overlap can also be responsible for the broad and not clear glass transition in PVA 88 blends. PVA 88 blends present a lower degree of crystallinity than PVA 99 blends, which results in the approximation of the amorphous and amorphous–crystalline relaxation processes. A broad shoulder in the temperature range between 45°C and 75°C for a PVP concentration of 60 wt% is in accordance with the DSC [6], which showed that the blends presented a larger number of microenvironments. The blend containing

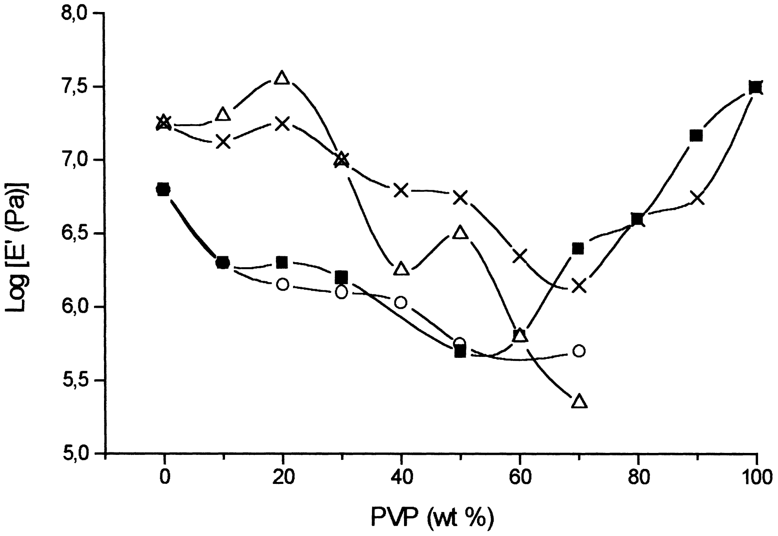

Fig. 3. Storage modulus (E') at 200°C as a function of the blends composition: (×) PVA 99/PVP 360; (△) PVA 99/PVP 10; (■) PVA 88/PVP 360; (○) PVA 88/PVP 10.

90 wt% of PVP 360 presented a broader relaxation range, between 50°C and 120°C, indicating a high density of interactions in this composition, as observed by DSC. The glass transition shifts to higher temperatures with an increase in the PVP concentration.

3.2. Storage modulus behaviour

The storage modulus (E') as a function of the temperature for the blends: PVA 99/PVP 10, PVA 99/PVP 360, PVA 88/PVP 10 and PVA 88/PVP 360 is shown in Fig. 2.

The E' modulus for PVA 99 (Fig. 2(a) and Fig. 2(b)) drops at 84°C due to the glass transition process followed by two falls: at 226°C due to the melting of the crystalline region and a second one between Tg and Tm at 140°C. A similar profile was observed in PVA 88 (Fig. 2(c) and Fig. 2(d)), but in this case the Tg occurs at 75°C and Tm at 184°C, and the drop of the E' modulus value between Tg and Tm is more pronounced in PVA 88 (10^2 Pa) than in PVA 99 (10 Pa) due to the higher degree of crystallinity of the PVA 99, which acts as a reinforcement.

The curve concerning PVP 360 (Fig. 2(b) and Fig. 2(d)) shows a single fall in the E' modulus value of ca. 10^4 Pa in the glass transition region at 181°C.

The E' modulus values as a function of the blends composition at 200°C for the four pairs of blends are shown in Fig. 3. Basically we can analyze the influence of two factors on the E' modulus at the temperatures between the Tg and Tm: PVP molecular weight and PVA hydrolysis degree. Blends with PVA 88 exhibit a lower crystallinity degree than the corresponding PVA 99 blends [6] and as consequence, the modulus at 200°C is lower for the former one.

The E' versus composition curves for PVP 360 blends exhibit a minimum. At PVP concentrations lower than this minimum the mechanical behavior of the blends is governed by the PVA crystalline phase. However, at higher concentrations of PVP, the mechanical behaviour can be attributed to the high stiffness of the PVP 360 chains, and their entanglements, which make the reptation processes in the material more difficult. Therefore, the E' modulus behaviour in the region between the glass transition and the fusion is governed by the PVA crystallinity and the content of PVP 360.

The influence of lower molecular weight PVP on the E' modulus behaviour can also be observed. The small PVP 10 chains, in spite of its stiffness, did not improve the mechanical resistance of the blends, favoring the reptation process of the chains. The reptation was characterized by the accentuated fall in E' modulus values at temperatures above Tg. The E' modulus for PVP 10 blends decreased with rise in PVP concentration. These curves did not show a minimum as in the corresponding curves of PVP 360 blends. In these cases, the mechanical behaviour of blends containing PVP 10 was predominantly governed by the PVA crystallinity.

4. Conclusions

The DMA results confirmed the miscibility of PVA/PVP blends. By this technique the detection of the secondary relaxations, which were not observed by DSC, was also possible. The analysis of secondary relaxations made the attribution to the amorphous and amorphous–crystalline phase possible.

Both the crystalline phase of PVA and the PVP 360 chains act as a reinforcement on the mechanical properties as shown by the E' modulus dependence on the blends composition. At the same time, PVP 10 facilitates chain reptation, in spite of being stiffer than PVA.

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