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Miscibility behaviour of ethylene vinyl acetate/Novolac blends

Nafaa Mekhilef* and Pavlos Hadjiandreou†
Plastics and Rubber Engineering Department, Algerian Institute of Petroleum, Boumerdes, 35000 Algeria
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Blends of ethylene vinyl acetate (EVA) resin, containing different amounts of vinyl acetate, and phenolic resin (Novolac type) were characterized by i.r. spectroscopy and differential scanning calorimetry (d.s.c.). The blends were prepared in the melt state at 130°C in a batch mixer. The compositions ranged from 20 to 80 wt% Novolac. Miscibility behaviour was investigated through i.r. spectroscopy which was focused on the region of the spectra corresponding to the stretching frequency of carbonyl groups of vinyl acetate. The addition of Novolac to EVA resins was found to result in strong molecular interactions between their functional groups, resulting in a splitting of the i.r. spectrum corresponding to the carbonyl group of EVA into two bands. Moreover, the absorption band of the carbonyl groups of EVA is shifted in the blends to lower wavenumber values by approximately 30 cm^{-1}. D.s.c. analysis has shown a total miscibility of the components for the whole range of composition, with a positive deviation from the Fox equation. However, for certain compositions, Kwei's equation was found to fit well with the experimental data. The results showed an improved compatibility between Novolac and EVA resin, an outcome of the specific interactions between the hydroxyl groups of Novolac and the carbonyl groups of EVA. It was also shown that no chemical reaction occurred between blend components, even at high temperature (180°C).

(Keywords: ethylene vinyl acetate; Novolac; miscibility)

INTRODUCTION

The range of applications achieved by phenolic resins is a result of their numerous properties coupled with low cost[1,2]. Although they are used extensively as ingredients in coatings and adhesives[3], their combination with relatively high molecular weight polymers has been restricted to solutions only[4,5]. The phenolic resin Novolac (PF) is a low molecular weight (600–1500) synthetic polymer having polynuclear phenols linked by *o*- and *p*-methylene groups[1]. Certain substituted Novolac resins are found to be miscible with a number of polar polymers containing carbonyl or carbonate groups. The latter groups are characterized by their ability to form hydrogen bonds with Novolac as evinced by shifts in the i.r. absorption spectra of many polymers[4]. Other works have shown that a few Novolac resins are compatible with ethylene vinyl acetate (EVA) copolymers[6] and polymers with similar structure such as poly(ethyl acrylate), poly(methyl methacrylate) and poly(vinyl acetate)[7–10]. This compatibility can be ascribed to the hydrogen bonding that might occur between the carbonyl and hydroxyl groups[11]. The degree of compatibility is dependent on various parameters, such as the solubility parameters of the components, which in turn depend on the dipole moment of the components. The dipole moment can only exist in the presence of polar side groups such as carbonyl, hydroxyl and amide side groups[12].

Several workers[10–12] have studied the interactions between polymers containing electron donor and electron acceptor groups using i.r. spectroscopy. The strength of these interactions is estimated using a graphical method based on measurements of the area of the peaks corresponding to the vibration band of the carbonyl group of the EVAs. Moreover, others have studied the compatibility of polymers involving molecular interaction using thermal methods[13–15], by employing theoretical predictions of glass transition temperature (T_g) as a function of composition. The T_g–composition behaviour can be well interpreted in terms of specific intermolecular forces acting between the functional groups of polymers.

In this work, we report the degree of compatibility between EVA and phenolic resins of Novolac type (PF) using i.r. spectroscopy and differential scanning calorimetry (d.s.c.). The former technique examines the presence of hydrogen bonds[8,9], whereas the latter demonstrates the behaviour of the T_g as a function of the blend composition and intermolecular forces. The correlation between these forces and the T_g–composition curves can be obtained using different models based on simple additivity rules or on specific assumptions such as the discontinuity of specific volume in miscible polymer blends.

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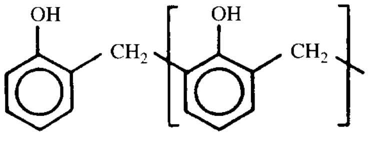
*To whom correspondence should be addressed. Present address: Chemical Engineering Department, Ecole Polytechnique de Montréal, PO Box 6079, Stn Centre ville, Montreal, Quebec, H3C 3A7 Canada

† Present address: Fuji Film Hellas SA, 1, IHous & AG, Anargiron Str., GR 175 64, Athens, Greece

EXPERIMENTAL

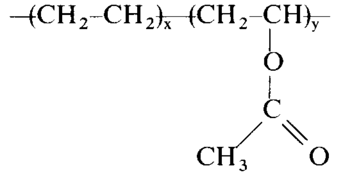
Materials

Phenolic resin (*PF*). This commercial phenol formaldehyde of Novolac type is synthesized from a molar excess of phenol with formaldehyde (commonly 1.25:1) under acidic conditions. Its softening point ranges from 80 to 100°C and the water content is estimated to be 4% by weight.



Structure of Novolac

Ethylene vinyl acetate (*EVA*). Five grades of EVA copolymers containing 14, 18, 20, 28 and 50% by weight vinyl acetate (VA) were used. They were provided by Exxon (14%, 18%), ESSO (20%), DuPont (28%) and Bayer (50%). Some of the copolymer characteristics are reported in *Table 1*.



$$-(CH_2-CH_2)_x-(CH_2-\underset{\substack{|\\ O\\ |\\ C(=O)CH_3}}{CH})_y-$$

Structure of ethylene vinyl acetate

Blend preparation

The phenolic resin was dried at 60°C for 24 h under vacuum prior to use. Then, blends containing 20 to 80% (w/w) PF were prepared in the melt state in a Brabender mixing chamber (MB 30H) with no. 6 rotors counter-rotating at 45 rev min^{-1} for a period of 20 min. The mixing head was heated to 130°C by an oil circulating system controlled automatically by a thermocouple. An additional blend was prepared with EVA14 (EVA14/PF 75/25) at two temperatures (130 and 180°C) for the extraction test.

I.r. spectroscopy

Sample preparation. Two different methods were used to prepare the samples. Because some of the blends (PF-rich) were 'brittle', it was necessary to grind and mix them with KBr powder to produce disc-like samples after cold mixing. For other blends which were more or less flexible (EVA-rich), it was possible to form a film by pressing a small amount of the blend between two KBr windows. Care was taken in using the KBr powder and windows. Reference spectra were acquired in order to confirm the absence of any residual moisture in the KBr salt. Moreover, they were used as references while acquiring spectra for the different samples in order to obtain data corresponding to the samples only.

Table 1 Characteristics of the EVA copolymers

	EVA14	EVA18	EVA20	EVA28	EVA50
VA content (%)	14	18	20	28	50
Density (g cm^{-3})	–	0.927	0.940	0.978	0.997
MFR (g/10 min)[a]	7.3	1.5	21.8	4.6	5.7
Crystallinity (%)	37	34	30	22	0
Softening point (°C)	67	–	57	–	–

[a] Melt flow rate

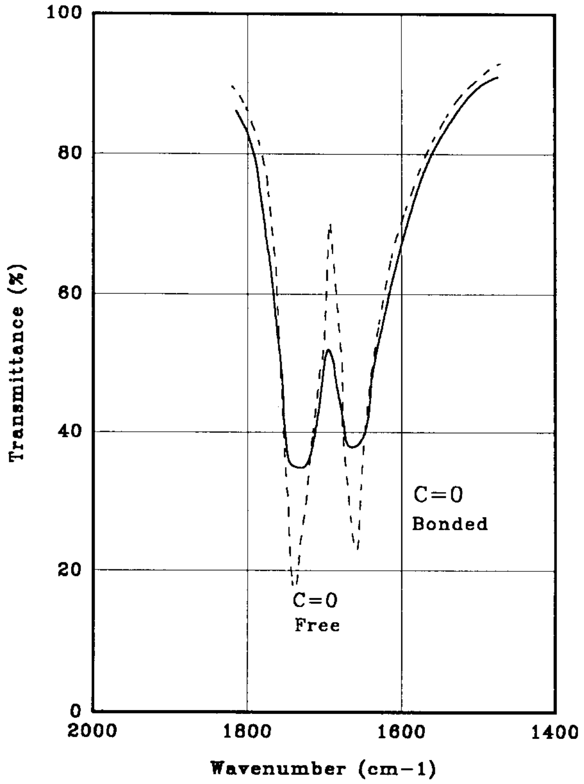


Figure 1 Schematic of a typical i.r. spectrum of an EVA/Novolac blend (curve resolving technique)

Characterization. I.r. spectroscopy was performed on all blends as well as on the raw materials to detect any possible physical interaction that might occur during blending. The i.r. equipment used was a Beckman model 4260 scanning at 4 cm^{-1} min^{-1}. Then, the extent of interaction between the functional groups of EVAs and Novolac was calculated using the graphical method. This method relies upon measuring the surface area under the peak corresponding to the hydrogen-bonded carbonyl groups of EVA *versus* the surface area under the peak of free carbonyl groups, as shown in *Figure 1*. The measured extent of interaction is based on the absorbance of the bands corresponding to the free carbonyl groups and to the hydrogen-bonded carbonyl groups according to the Beer–Lambert law:

$$A_f = a_f \varepsilon C_f \tag{1}$$

and

$$A_b = a_b \varepsilon C_b \tag{2}$$

where A is the absorbance (area), a the absorptivity of the band corresponding to the free (f) and hydrogen-bonded (b) C=O group, ε the thickness of the sample and C the fraction of the corresponding group. The thickness of the sample being constant in the blend, the relative extent of interaction can be estimated as:

$$\frac{1-C_b}{C_b} = \frac{a_b}{a_f}\frac{A_f}{A_b} \tag{3}$$

or

$$\%\mathrm{C{=}O}_{(\mathrm{bonded})} = k\frac{A_\mathrm{b}}{A_\mathrm{f}} \tag{4}$$

Extraction test

This test was performed in order to detect the presence of any chemical reaction. It was carried out on one composition of the blend containing EVA with the lowest VA content (i.e. 14% by weight). This choice is based on the fact that EVA with relatively high VA content is fairly soluble in acetone. Owing to the difficulty in finding a selective solvent for PF with these grades, the test was limited to EVA14/PF 75/25 blended at 130 and 180°C. The solutions contained 2% by weight of the blends and were stirred continuously for 36 h at room temperature.

Differential scanning calorimetry

D.s.c. was conducted on all blends and raw materials. The equipment used was a Perkin–Elmer DSC-4 at a heating rate of 20°C min^{-1}. The T_g values were recorded during the second scan to remove residual phenol that might exist in Novolac, and the thermal history due to blending.

RESULTS AND DISCUSSION

I.r. spectroscopy

The i.r. spectra in the region of 1700 to 1800 cm^{-1} for the different EVA/PF blends are given in *Figures 2* to *5*. The spectra have been expanded four times for the sake of clarity. They are obtained either by direct measurement on the blend samples on KBr discs or blended with small amounts of the blends. Therefore, the measured transmittance may vary from one sample to the other. Regarding the spectra of the KBr powder, a quantitative analysis can be done to measure the extent of interaction between the C=O groups contained in the copolymers and the O–H groups contained in the Novolac. Errors obtained in these calculations are primarily due to experimental

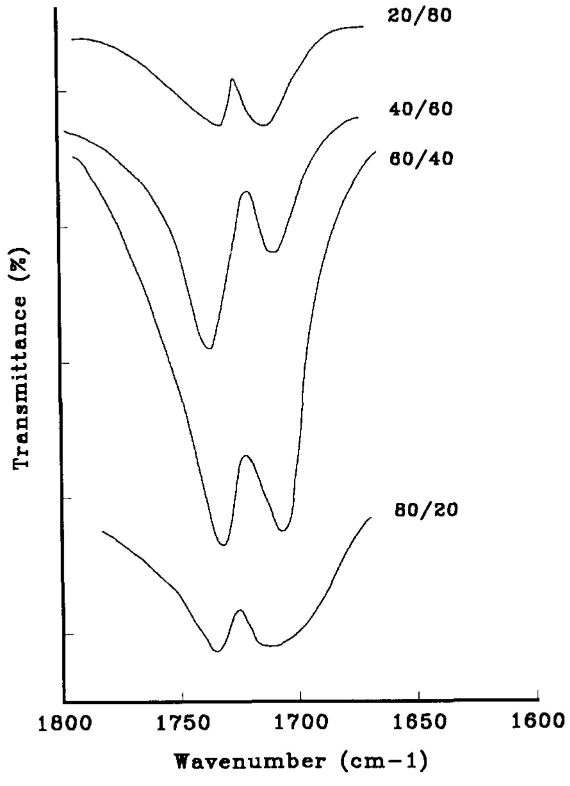


Figure 2 I.r. spectra of the EVA18/PF blends

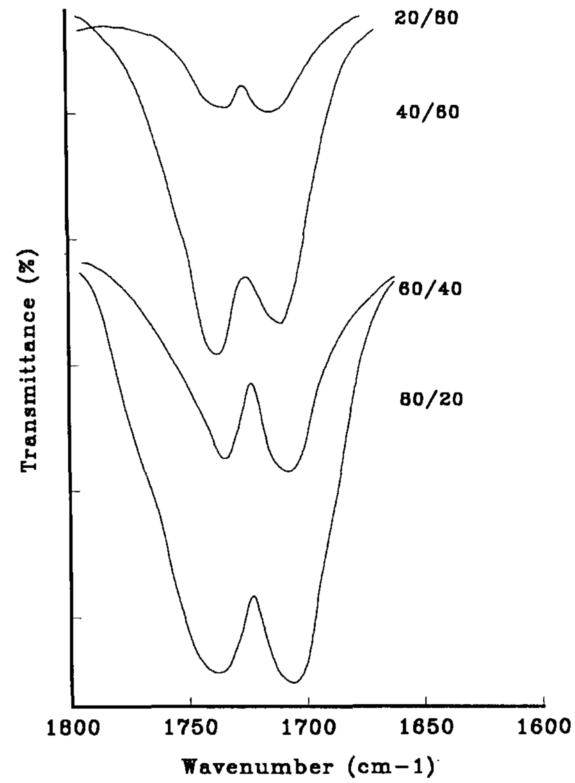


Figure 3 I.r. spectra of the EVA20/PF blends

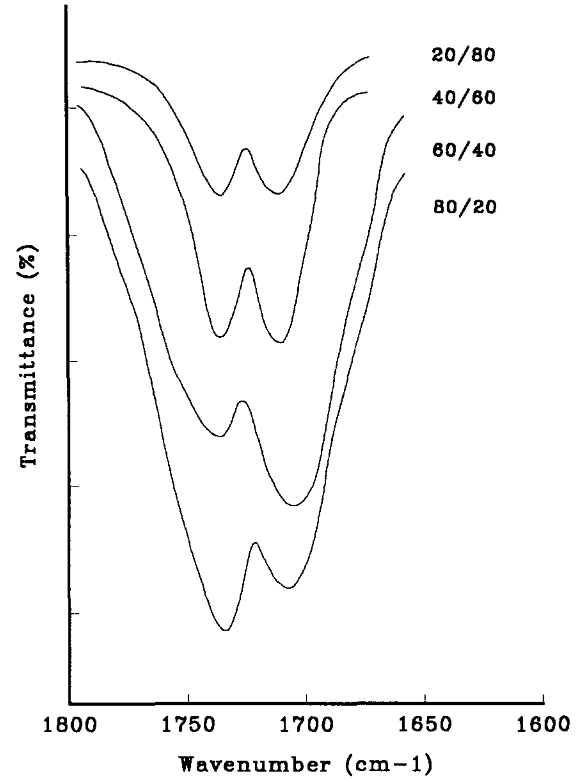


Figure 4 I.r. spectra of the EVA28/PF blends

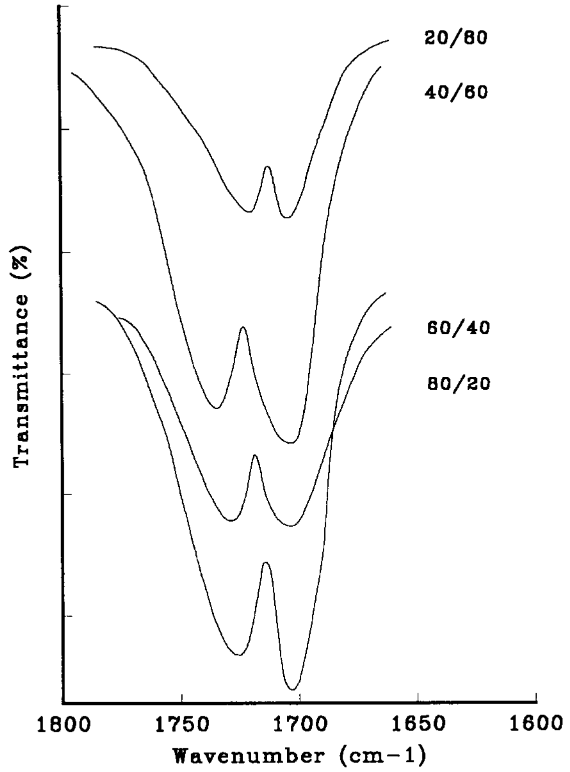


Figure 5 I.r. spectra of the EVA50/PF blends

protocol, i.e. a little difference in thickness of the samples with respect to that of the reference, curve resolving technique and measurement of areas under the peaks.

The carbonyl stretching vibration has proven to be an excellent probe for molecular mixing in a number of polymer blends[13]. Therefore, it seemed pertinent to use the carbonyl stretching vibration through its sensitivity to hydrogen-bond interactions. These interactions are believed to have a considerable influence on polymer compatibility. It is observed that the absorption of the carbonyl group of EVA in the blend, usually occurring at 1738 cm^{-1} for pure EVA, is shifted to lower wavenumber values by approximately 30 cm^{-1}, resulting in two bands. In fact, part of the carbonyl absorption band of EVA shifts from 1740 to about 1710 cm^{-1} when the copolymer is mixed with Novolac. This observation is in line with the findings of a previous study[16], which is indicative of the presence of interactions between the two components in the mixture. On the other hand, a slight difference in the shift of carbonyl absorption is observed for different EVA copolymers.

The quantitative analyses of the treated spectra (curve resolved) are summarized in *Tables 2* to *5*, where the shift in the wavenumbers, the wavenumber of the free carbonyl groups, the wavenumber of the hydrogen-bonded C=O groups and the extent of interaction calculated using equation (4) are reported as a function of blend composition. In the case of blends containing EVA18 (*Table 2*), the shift to lower wavenumbers varies from 28 to 35 cm^{-1} as the EVA content increases from 20 to 80% by weight. The extent of interaction increases as the number of carbonyl groups increases in the blend. For the blends containing EVA20, the shift ranges from 17 to 35 cm^{-1} with increasing EVA content, while the extent of interaction is kept almost constant except for the 60/40 blend, which appears to be anomalous (*Table 3*).

For higher VA content (i.e. EVA28), the shift ranges from 27 to 30 cm^{-1} while the extent of interaction shows a maximum for the 60/40 blend. This may be due to a saturation concentration in terms of carbonyl and hydroxyl groups in EVA and Novolac blend. Above this VA content (i.e. EVA50), the shift varies from 23 to 28 cm^{-1} and the extent of interaction shows a maximum at the lowest EVA content in the blend (20/80).

For the EVA18 blends, the percentage of hydrogen-bonded carbonyl groups increased almost linearly with increasing EVA content. This is ascribed to the greater amount of carbonyl groups present in the blend. However, in the case of blends with a similar VA content (EVA20), the percentage of hydrogen bonding seemed to be insensitive to the composition except at 60/40, where it reaches the minimum. With almost the same VA

Table 2 Wavenumbers of free and hydrogen-bonded carbonyl groups and extent of interaction of EVA18/PF blends

Blend composition	Carbonyl wavenumber (cm^{-1})			H-bonded carbonyl (%)
	W_{free}	$W_{H\text{-bonded}}$	$W_f - W_{H\text{-b}}$	
20/80	1740.0	1706.0	34.0	29.9 ± 4.0
40/60	1736.0	1703.0	33.0	34.4 ± 3.6
60/40	1734.0	1706.0	28.0	51.5 ± 1.2
80/20	1748.0	1713.0	35.0	60.2 ± 3.3
100/0	1740.0	–	–	–

Table 3 Wavenumbers of free and hydrogen-bonded carbonyl groups and extent of interaction of EVA20/PF blends

Blend composition	Carbonyl wavenumber (cm^{-1})			H-bonded carbonyl (%)
	W_{free}	$W_{H\text{-bonded}}$	$W_f - W_{H\text{-b}}$	
20/80	1733.0	1716.0	17.0	46.0 ± 3.9
40/60	1735.0	1708.0	27.0	43.7 ± 1.7
60/40	1736.0	1711.0	25.0	30.0 ± 1.2
80/20	1738.0	1703.0	35.0	43.4 ± 0.9
100/0	1740.0	–	–	–

Table 4 Wavenumbers of free and hydrogen-bonded carbonyl groups and extent of interaction of EVA28/PF blends

Blend composition	Carbonyl wavenumber (cm^{-1})			H-bonded carbonyl (%)
	W_{free}	$W_{H\text{-bonded}}$	$W_f - W_{H\text{-b}}$	
20/80	1736.0	1709.0	27.0	46.9 ± 2.3
40/60	1735.0	1706.0	29.0	49.2 ± 1.5
60/40	1734.0	1704.0	30.0	57.9 ± 0.9
80/20	1735.0	1709.0	26.0	55.6 ± 0.8
100/0	1740.0	–	–	–

Table 5 Wavenumbers of free and hydrogen-bonded carbonyl groups and extent of interaction of EVA50/PF blends

Blend composition	Carbonyl wavenumber (cm^{-1})			H-bonded carbonyl (%)
	W_{free}	$W_{H\text{-bonded}}$	$W_f - W_{H\text{-b}}$	
20/80	1729.0	1706.0	23.0	64.8 ± 1.9
40/60	1733.0	1705.0	28.0	55.6 ± 2.0
60/40	1751.0	1740.0	11.0	51.5 ± 2.1
80/20	1734.0	1710.0	24.0	53.5 ± 1.5
100/0	1740.0	–	–	–

Table 6 Experimental results for solvent extraction at room temperature for EVA14/PF blended at 130 and 180°C

Fractions vs. materials	Composition EVA14/PF	Soluble part (%)	Insoluble part (%)
Novolac (PF)	0/100	90.8	9.3
EVA14	100/0	1.2	98.3
EVA14/PF (130°C)	75/25	25.6	74.4
EVA14/PF (180°C)	75/25	23.8	76.2

content as before one would expect the same behaviour (i.e. an increase in the percentage of hydrogen-bonded carbonyl groups), but this is not the case because the molecular weight might be different.

Above 20% VA, the percentage of hydrogen-bonded carbonyl groups increases with increasing EVA content in the blend, reaching a maximum at 60/40, which confirms the observations made previously. It is of interest to note that such a maximum also exists in the case of EVA18. This is not the case for EVA20, suggesting that the latter results may be associated with lower molecular weight. Hence, these maxima at 60% by weight EVA cannot be explained in terms of the ratio of carbonyl groups in EVA and hydroxyl groups in Novolac. Presumably, the higher VA content (50%), would give the maximum percentage of hydrogen-bonded carbonyl groups. This is observed for the 20/80 blend, confirming the existence of a greater number of carbonyl groups than of hydroxyl groups of Novolac (*Table 5*). It appears that above a certain VA content, the strength of hydrogen-bond interaction decreases. This could be explained from the saturation concentration, i.e. an equilibrium which does not necessarily correspond to a total contribution of the functional groups, but rather to an equilibrium reached upon cooling the blends, where hydrogen bonds are formed and destroyed instantly[6,17].

Solvent extraction

Based on different solubilities of homopolymers, acetone was selected as the solvent. As mentioned earlier, the test was carried out on blends containing EVA with low VA content (EVA14). The study was performed on the EVA14/PF 75/25 blend prepared at 130 and 180°C, as well as for raw materials.

Table 6 shows that the commercial Novolac used in this study is almost soluble in acetone (>90%), whereas EVA14 is insoluble. While performing the extraction test, the weight fractions of soluble and insoluble parts of the prepared blends are found to correspond to the composition of the blends. This suggests that the grafting or partial crosslinking of Novolac to EVA does not arise at either mixing temperatures of 130 or 180°C. Hence, it confirms that no chemical reaction has taken place between the blend components.

Differential scanning calorimetry

D.s.c. was carried out on virgin materials and on the different blends. It should be noted that EVA18, 20 and 28 are partially crystalline materials whereas EVA50 and Novolac are amorphous. This has been verified from d.s.c. thermograms. For the blends, the endothermic peaks corresponding to the melting point for relatively low VA copolymers are not found. This shows that the blends are either amorphous or possess a very low degree of crystallinity which is not detected by this technique. It is known that the crystallinity of the copolymers is due to the presence of well formed structures of ethylene groups which are randomly distributed. Having blended with the amorphous and bulky structure of Novolac, the crystalline part is dispersed within the amorphous phase of the blends, rendering the process of crystallization very difficult upon cooling. Therefore, one should consider hypothetically the T_g of the amorphous phase of EVA rather than that of the semicrystalline copolymer. Stein *et al.*[18] studied the morphology of binary blends by using X-ray and optical techniques, where one or both phases can crystallize. They showed different possible morphologies of the blend that can be obtained while suggesting that the morphology is highly dependent on the compatibility of the amorphous polymers, their crystallizability, diffusion and kinetic factors. Below a certain degree of crystallinity in one of the phases, the blend does not show any crystallization upon cooling. On the other hand, Painter *et al.*[19] studied the effect of hydrogen bonding on the melting point depression in polymer blends where one phase crystallizes. They reported that in this case the blends exhibit single T_gs, suggesting total miscibility of the amorphous parts in each phase and also associated with melting point depression[20–22]. They also showed that the melting point depression can be predicted as a function of blend composition. Based on the d.s.c. thermograms obtained in our case, the blends are apparently amorphous and thus the amorphous part of the copolymers interacts with Novolac and significantly reduces the crystallinity of the blends. More rugged techniques are required to investigate the residual crystallinity, if any, within the blends.

Figures 6 to *9* show the T_g–composition curves of EVA18/PF, EVA20/PF, EVA28/PF and EVA50/PF blends. The T_g corresponding to the amorphous phase of the pure copolymer decreases with increasing VA content. In all cases, a single T_g is observed for all blend compositions, suggesting that these systems are miscible,

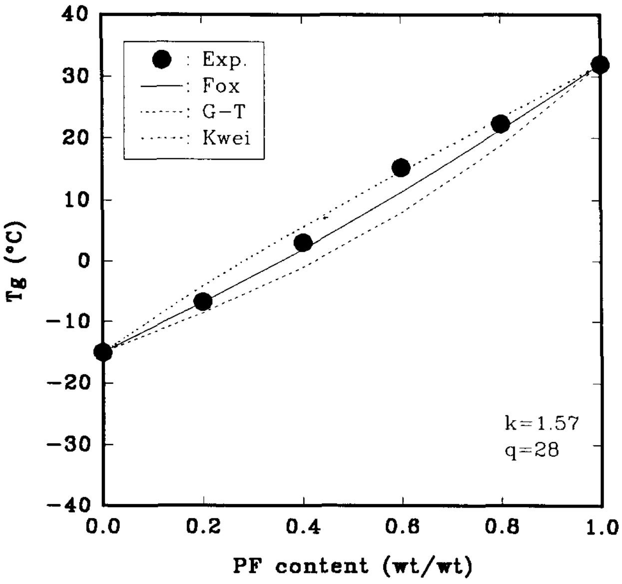


Figure 6 Experimental and theoretical predictions of T_g *versus* composition of EVA18/PF blends

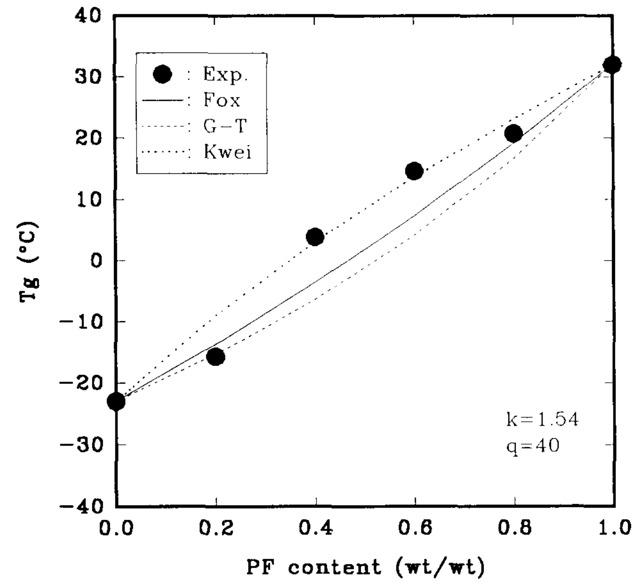


Figure 7 Experimental and theoretical predictions of T_g *versus* composition of EVA20/PF blends

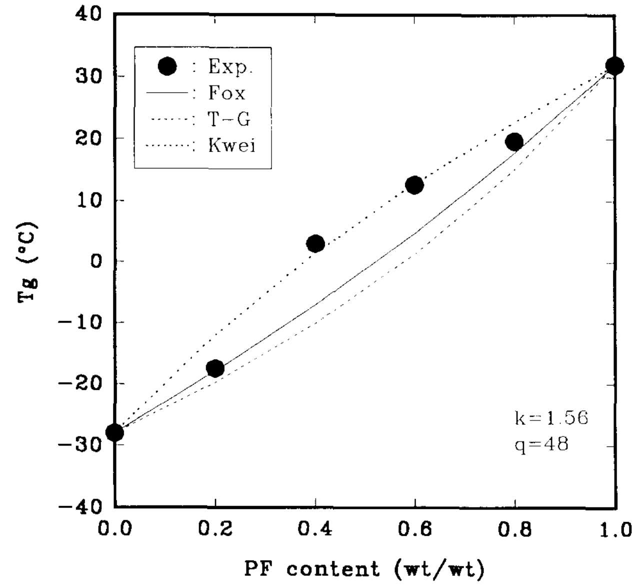


Figure 8 Experimental and theoretical predictions of T_g *versus* composition of EVA28/PF blends

at least in the amorphous phase of the blend. In addition, no apparent microphase separation is observed as the width of the transition zone is just intermediate between those of the individual components. For the EVA18/PF blend, the results obtained are compared to those calculated by the Fox equation (indicated in *Figure 6* by a continuous line):

$$\frac{1}{T_{gb}} = \frac{\phi_1}{T_{g1}} + \frac{\phi_2}{T_{g2}} \tag{5}$$

where ϕ_1 and ϕ_2 are the weight fractions of EVA18 and PF, respectively. As can be seen from *Figure 6*, the experimental data give a slightly positive deviation relative to the Fox equation[23]. We note that this deviation is unusual except in the case of a few polymer pairs[14,24,25]. The dashed line in *Figure 6* represents the Gordon–Taylor equation which assumes no discontinuity in specific volume near the T_g and is given by:

$$T_{gb} = \frac{\phi_1 T_{g1} + \phi_2 T_{g2}}{\phi_1 + k\phi_2} \tag{6}$$

with

$$k = \frac{v_2 \Delta\alpha_2}{v_1 \Delta\alpha_1} \tag{7}$$

where v_1 and v_2 are the specific volumes of the components, and $\Delta\alpha_1$ and $\Delta\alpha_2$ are the differences between the thermal expansion coefficients at the glassy and liquid state of both materials. These data are given in *Table 7*. Since the T_g of each polymer is close to the ambient temperature, we assumed that the specific volumes are not different from those obtained at room temperature. According to *Figure 6*, the Gordon–Taylor equation did not yield a better fit with the experimental data. This curve could be obtained using the validity of the Simha–Boyer model stating that $\Delta\alpha T_g = 0.115$ (ref. 26). However, if we consider the extended Gordon–Taylor model proposed by Kwei[5], we notice that the agreement is much better, at least for the 40/60 blend composition:

$$T_{gb} = \frac{\phi_1 T_{g1} + \phi_2 T_{g2}}{\phi_1 + k\phi_2} + q\phi_1\phi_2 \tag{8}$$

where q is a fitting parameter related to the strength of interaction. In the case of the EVA18/PF blend and with a value of $k = 1.57$, we obtain a value of $q = 28$, indicating the presence of strong intermolecular forces. These

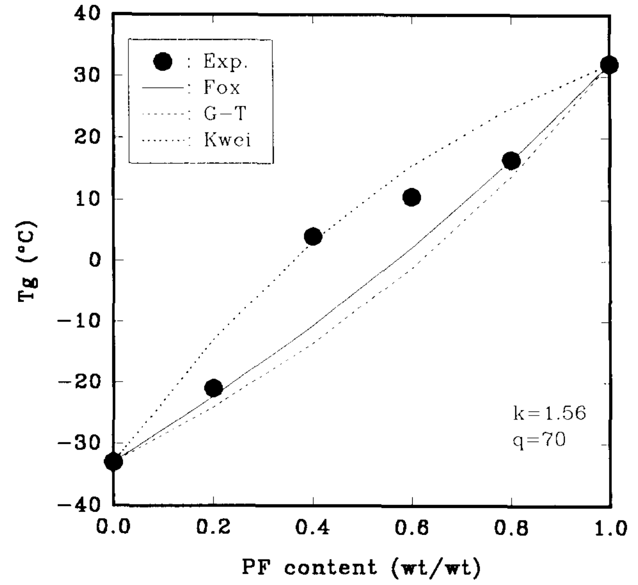


Figure 9 Experimental and theoretical predictions of T_g *versus* composition of EVA50/PF blends

Table 7 Parameters used in Gordon–Taylor and Kwei equations

Material	T_g (°C)	$\Delta\alpha \times 10^4$ (°C^{-1})	v at 25°C (cm^3 g^{-1})	k
PF	32.0	3.77	2.000	
EVA18	−15.0	4.45	1.079	1.57
EVA20	−23.0	4.60	1.064	1.54
EVA28	−28.0	4.71	1.022	1.57
EVA50	−33.0	4.80	1.007	1.50

findings are also in line with those reported by other authors for systems containing Novolac resins[4,5], EVA copolymers[4,25] and other polymers[13,14,25].

In the case of other blends with different VA contents, similar results are obtained, at least for the blends containing 40 and 60% by weight Novolac. For the EVA20/PF blend, q is 40 for a k value of 1.54, whereas for EVA28/PF and EVA50/PF the q values are 48 and 70 for almost the same value of k, i.e. 1.57 and 1.56, respectively. Now if we consider that k has no effect, as is the case with different EVA copolymers, it is observed that q increases with the VA content in EVA for each blend. This raises the question of whether any relationship exists between the strength of the intermolecular forces measured by i.r. and q. The fact that q values are found to increase with the VA content is merely a coincidence. But if an attempt is made to correlate the extent of interaction measured through the hydrogen-bonded carbonyl groups of EVA with q, then one may find a rationale behind the relationship. Lu and Weiss[27] found that the T_g of a miscible blend of sulfonated polystyrene with nylon-6 can be predicted using the Lu–Weiss model[28], applying the Flory–Huggins segmental interaction parameter χ which in turn is calculated from the Nishi–Wang equation[29]. The positive deviation of the experimental results is attributed to strong intermolecular interactions between the two polymers. On the other hand, Kwei[5] studied the T_g–composition relationship in Novolac poly(methyl methacrylate), both in isotactic and syndiotactic form, and observed a similar behaviour. The term q, which represents the amount of specific interactions in the mixture, is interpreted as a contribution of the hydrogen bonding which is well identified by i.r. spectroscopy. This enables us to use the term q as a probe to measure the strength of hydrogen-bond interactions. This is not surprising since q increases with VA content in the blend which is further associated with the number of C=O groups present. Therefore, q varies in the same manner as the extent of interaction, which explains why the best fit of Kwei's equation is found for certain compositions only. It is clear that the formation of hydrogen bonds between Novolac and different EVA copolymers is influenced by the number of C=O groups in EVA and also by the mobility of the VA side group.

CONCLUSIONS

I.r. spectroscopy is successfully employed to detect and identify the presence of specific interactions occurring between EVA and Novolac resins, as observed by the splitting of the carbonyl stretching band into two distinct absorption bands approximately 30 cm^{-1} apart.

The amount of hydrogen-bonded carbonyl groups increases with EVA content as well as the VA content. However, there is a saturation point above which the number of carbonyl groups in the blend becomes greater than the number of hydroxyl groups of the Novolac resin. In other words, the hydrogen bond is determined by the mobility of the carbonyl group in the EVA chain since the bridged phenolic rings in the Novolac are very rigid. Moreover, differential scanning calorimetry has shown that the T_g exhibits a positive deviation of the experimental results compared to the Fox equation for all the blends. The Gordon–Taylor equation did not show a better agreement using k values calculated using the Simha–Boyer model. However, Kwei's equation gives the best agreement with the experimental results. The value of q, which represents the strength of the hydrogen bonds, is found to increase with increasing VA content in the blend, regardless of the molecular weight. The variation of q with VA content may be related to the extent of interaction between the hydroxyl and carbonyl groups of Novolac and EVA, respectively.

The present work has also shown that i.r. spectroscopy is undeniably an excellent method for studying the mixing of polymers at the molecular level in the condensed state.

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