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Effect of Cross-Linking on the Degree of Molecular Level Mixing in a Polymer Blend

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ABSTRACT: The results of a Fourier transform infrared study of different phenolic resin blends containing an ethylene–vinyl acetate (EVA) copolymer are presented. The EVA carbonyl stretching vibration is employed as a probe of molecular mixing through its sensitivity to intermolecular hydrogen-bonding interactions. In the absence of cross-linking, novolac and model poly(vinylphenol) blends with EVA form essentially single-phase systems. These blends may be cycled up and down in temperature, and the fraction of hydrogen-bonded carbonyl groups observed is determined primarily by the strength of the intermolecular interaction, the blend composition, and the temperature, in other words, an equilibrium process. In contrast, when the phenolic resin undergoes reactions leading to increases in molecular weight, branching, and cross-linking during the heating cycle, phase separation occurs. The fraction of hydrogen-bonded EVA carbonyl groups observed is significantly less than that expected from equilibrium considerations. The ramifications of these results to semiinterpenetrating networks and polymer mixing in general are discussed.

Introduction

Although we have a vested interest in infrared spectroscopy and might be excused for some slight bias in favoring the technique, under advantageous conditions it is undeniably an excellent method for studying the mixing of polymers at the molecular level in the condensed state. The infrared probe size is at the level of a few angstroms, and information concerning the extent of mixing may be gained from an analysis of isolated normal modes that are sensitive to perturbations arising from specific intermolecular hydrogen-bonded interactions. The carbonyl stretching vibration, for example, has proven to be an excellent probe of molecular mixing for a number of polymer blends.[1] In poly(4-vinylphenol) (PVPh) blends with poly(vinyl acetate), ethylene–vinyl acetate copolymers, and polylactones,[2-4] it was a reasonably straightforward task to distinguish between and quantitatively measure those carbonyl groups that were and were not hydrogen bonded to the phenolic hydroxyl groups. The fraction of hydrogen-bonded carbonyl groups was measured as a function of temperature, and these results compare favorably to those calculated from a simple equilibrium model.[5]

The studies presented in this paper, which concern blends composed of an ethylene–vinyl acetate copolymer containing 70 wt % vinyl acetate (EVA[70]) with different phenol–formaldehyde (PF) resins, represent a logical, albeit rather complicated, extension to our previous work. The EVA[70] carbonyl stretching vibration will still be our infrared probe of molecular mixing through its sensitivity to intermolecular hydrogen bonding to the PF phenolic hydroxyl group. In this case, however, the PF resins may be cross-linked, potentially forming a semiinterpenetrating network (semi-IPN).[6,7] Somewhat naively, we postulated that, given the relatively strong intermolecular interaction involved (about -5 kcal mol^{-1}),[2] it should be possible to form a truly "miscible" semi-IPN, where, conceptually, the linear EVA[70] chains would "snake" in and out of the three-dimensional network, forming, at any instant of time, the maximum number of intermolecular hydrogen-bonding interactions dictated by equilibrium considerations. We recognized that the small entropy of mixing that occurs in high molecular weight linear polymer–polymer blends will be even less if one of the polymers undergoes cross-linking. Nevertheless, we were optimistic that a miscible semi-IPN could be formed, given the favorable enthalpy of mixing. As we will see, this optimism was unfounded.

Homogeneous IPNs have been reported for epoxy/acrylic systems[8,9] on the basis of thermal analysis and dielectric relaxation studies. This system should not be confused, however, with an interpenetrating network of an acrylic polymer intertwined with a cross-linked epoxy resin. In our opinion, it is better described as an epoxy–epoxy IPN where two different epoxy networks are formed by dissimilar chemical mechanisms, a free-radical reaction through an acrylic end group and a condensation reaction through an epoxy end group. A semi-IPN based upon an epoxy resin with polycaprolactone (PCL) has also been studied,[10] and infrared spectroscopy was one of the techniques employed. For the amine-cured epoxy system it was concluded that the semi-IPN with PCL was partially miscible.

Miscible IPNs have been reported by Frisch and coworkers,[11,12] who prepared linear blends, semi-IPNs, and IPNs of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) which exhibited single T_gs that varied systematically with composition. In addition, no evidence of phase separation was seen in the electron microscope. To a large extent, however, the probe size of the experimental method used to study these complex mixtures dictates whether or not a system is deemed

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Table I
Curve-Fitting Results for 80:20 PVPh-EVA[70] Blend

T, °C	"free" C=O			H-bonded C=O			fraction[a] H-bonded
	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_F	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_{HB}	
30	1737	19	334	1707	33	1048	0.68
100↑	1738	19	337	1708	33	955	0.65
150↑	1738	19	362	1710	33	887	0.62
200	1739	19	365	1712	33	832	0.60
150↓	1738	19	364	1710	33	884	0.62
100↓	1737	19	339	1708	33	985	0.66
30↓	1736	19	289	1707	32	979	0.69

[a] Calculated from $(A_{HB}/1.5)/(A_F + A_{HB}/1.5)$; see text.

miscible. Questions relating to the possibility of microphase separation inevitably arise. Unfortunately, infrared spectroscopy, which potentially has the ideal probe size to study mixing of these polymers at the molecular level, appears impotent in such systems. The intermolecular interaction between the PPO and PS polymers is too weak to significantly perturb isolated normal modes that might be unambiguously used to determine the degree of mixing.

Experimental Section

Poly(4-vinylphenol), an amorphous polymer with a reported molecular weight M_n = 1500–7000 and a T_g of 130 °C, was purchased from Polysciences, Inc. The ethylene–vinyl acetate copolymer containing 70 wt % vinyl acetate (EVA[70]) was obtained from Mobay Chemical Co. It too is an amorphous polymer with a T_g of approximately 28 °C. Hexamethylenetetramine (HMT) and the two phenolic polymers, typical commercial resol and novolac resins that are described in more detail later, were obtained from Monomer–Polymer and Dajac Laboratories.

Samples were prepared for infrared analysis by casting thin films onto potassium bromide windows from a 2% w/v solution of the polymer blends in a common solvent. In all cases but one tetrahydrofuran (THF) was employed as the solvent. For the samples of the novolac–EVA[70] blends containing HMT, it was necessary to employ a mixed-solvent system, an 80:20 v/v dimethylformamide/methanol mixture, because of the insolubility of HMT in THF. With the exception of the resol blends, after the evaporation of the vast majority of the solvent at ambient temperature, all samples were pretreated at 100 °C under reduced pressure for 3–6 h to ensure the elimination of the solvent and any water. This has the added advantage of minimizing the effects of possible phase separation occurring as the solvent is evaporated, which is induced by differential affinities of the two polymers for the common solvent. The resol blends were not pretreated at elevated temperatures for reasons elaborated in the text. Instead, they were subjected to vacuum desiccation at room temperature for at least 12 h prior to study. In all cases, no absorptions attributable to the solvent were detected in the infrared spectra of the samples.

Infrared spectra were obtained on a Digilab FTS-15E Fourier transform infrared (FT-IR) spectrometer. A minimum of 64 scans at 2-cm^{-1} resolution were signal averaged and stored on a magnetic disk system. The spectrometer is internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}. Spectra recorded at elevated temperatures were obtained by using a heating cell mounted inside the sample compartment of the spectrometer. Temperature control was effected by a Micristar 828D digital process controller to a reported accuracy of ±0.1 °C.

Results and Discussion

PVPh Blends with EVA[70]. Before we become immersed in the details of the PF resin–EVA[70] blends, it is pertinent to review the FT-IR results obtained from the "model" PVPh–EVA[70] system.[2] PVPh is an atactic vinyl-type polymer that has the chemical repeating unit $-[CH_2CH(C_6H_4OH)]-$. Although there are significant differences in the chemical moieties present in PVPh and the PF resins, discussed in more detail later, the dominant intermolecular interaction of interest in blends with EVA[70] is identical, a hydrogen bond between the phenolic hydroxyl and the EVA carbonyl groups. EVA[70] can be used as a probe of molecular mixing because infrared bands attributed to carbonyl groups that are and are not hydrogen bonded to phenolic hydroxyl groups are well resolved and occur in a region of the spectrum free from other absorptions. This is illustrated in Figure 1, which shows the carbonyl stretching region for a sample of an 80:20 wt % PVPh-EVA[70] blend recorded as a function of increasing and then decreasing temperature. The two infrared bands occurring at about 1740 and 1710 cm^{-1} are attributed to "free" (non-hydrogen-bonded) and hydrogen-bonded carbonyl groups, respectively.[1-3] By use of an appropriate base line, the band envelope may be readily fitted to two Gaussian bands. A quantitative measure of the fraction of hydrogen-bonded EVA[70] carbonyl groups can now be obtained by employing the previously determined absorptivity ratio, a_{HB}/a_F = 1.5.[2] The results of such a procedure are summarized in Table I. It should be emphasized that the blend sample, which was prepared by casting a film from the common solvent THF, was pretreated by heating to 100 °C in a vacuum oven for 3 h before cooling to room temperature and subsequent recording of the infrared spectra. This was necessary to ensure complete removal of the solvent and to minimize phase separation through the so-called $\Delta\chi$ effect.[13,14] At room temperature approximately 68% of the EVA[70] carbonyl groups were found to be hydrogen bonded. This indicates a high degree of molecular mixing, and the measured value is in good agreement with our previous theoretical calculations based upon a single-phase equilibrium model.[5] The fraction of hydrogen-bonded carbonyl groups decreases as the temperature is raised (60% at 200 °C; see Table I) and recovers to the original

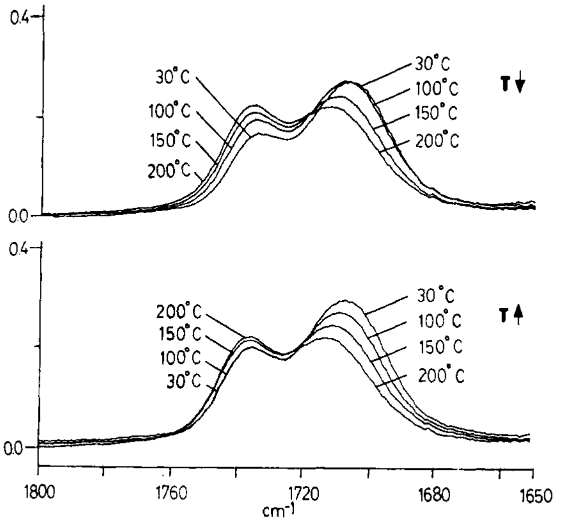

Figure 1. FTIR spectra of an 80:20 wt % PVPh-EVA[70] blend in the region from 1650 to 1800 cm^{-1}: (bottom) heating cycle; (top) cooling cycle.

Table II
Curve-Fitting Results for 80:20 Resole-EVA[70] Blend

	"free" C=O			H-bonded C=O			
T, °C	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_F	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_{HB}	fraction[a] H-bonded
		Temperature Study					
30	1736	19	518	1708	31	1460	0.65
100↑	1737	18	611	1711	31	1249	0.58
150↑	1739	19	839	1714	33	909	0.42
200	1740	20	1018	1717	39	674	0.31
150↓	1739	20	1121	1714	40	756	0.31
100↓	1739	20	1147	1713	41	789	0.32
30↓	1738	20	1124	1713	46	918	0.35
		Isothermal Curing at 150 °C					
150 (immed)	1737	19	957	1711	32	1759	0.55
quenched to room temp	1735	18	705	1707	33	2117	0.64
150 (5 min)	1738	19	684	1712	31	1043	0.50
quenched to room temp	1735	18	487	1708	31	1219	0.60
150 (30 min)	1738	19	1100	1713	33	1432	0.46
quenched to room temp	1736	18	611	1708	32	1283	0.57

[a] As in Table I.

value upon cooling to room temperature. This is consistent with an equilibrium process, the fraction of hydrogen-bonded carbonyl groups being determined by an equilibrium constant.[2,5] This facility to cycle up and down the temperature scale and obtain essentially the same fraction of hydrogen-bonded carbonyl groups at any given temperature will be important to our subsequent arguments.

Resol-EVA[70] Blends. A resol is a PF resin synthesized from phenol with a molar excess of formaldehyde (commonly a 1:(1.5-2) ratio) under alkaline conditions. A condensation reaction is performed, and the extent of reaction is limited by quenching before the gel point. Typical commercial resols have, on average, 3-4 aromatic rings per molecule. Methylol groups substituted on the aromatic rings and methylene bridges between the rings predominate, and both tend to be restricted to ortho and para positions. It is the presence of the methylol groups that permits the continuation of the polymerization process through the application of heat alone and eventually leads to gelation and a cross-linked network. The mechanism of cross-linking in resols is complex, and the interested reader is referred elsewhere for details.[15] In general, however, it is considered that the polymer network is composed primarily of phenolic rings linked together by methylene groups (with some ether and olefin moieties also present as bridges). Significantly, the phenolic hydroxyl groups are not consumed in the cross-linking reaction, and the total concentration of these groups may be assumed to be constant throughout the cross-linking reaction.

Let us now repeat the experiment described above on the PVPh-EVA[70] blend but substitute a resol for PVPh. A resol-EVA[70] blend sample was prepared as a thin film on a KBr window by casting from THF. In this case we wished to avoid the possibility of additional resol polymerization and/or cross-linking that might occur at elevated temperatures. Accordingly, the sample was placed under vacuum at room temperature for 12 h in order to remove the solvent. No evidence for residual THF was detected by infrared spectroscopy. Using this method of sample preparation, we risk some phase separation via the $\Delta\chi$ effect. This, however, is not a major cause for concern as we will demonstrate below.

The carbonyl stretching region of the infrared spectrum of an 80:20 wt % resol-EVA[70] blend sample is shown in Figure 2. Spectra that were recorded at 30, 100, 150, and 200 °C as the sample was being heated and at the same temperatures during cooling are presented on an absolute absorbance scale. Curve fitting to two Gaussian bands were performed on these spectral data in a manner identical with that described for the PVPh-EVA[70] system. The results are summarized in Table II. The result obtained from the spectrum of the resol-EVA[70] sample recorded prior to any heating is immediately gratifying. The frequency and breadth of the two bands are very much the same as those obtained for the PVPh-EVA[70] system (compare Tables I and II). As an aside, this suggests that intermolecular interactions involving the EVA[70] carbonyl groups with the methylol hydroxyls present in the resol are not significant. The phenolic hydroxyl-carbonyl interaction is energetically more favorable, and if there were significant involvement from methylol-carbonyl interactions, we would expect a spectral contribution at about 1720 cm^{-1},[16] which would most likely manifest itself through an overall broadening of the hydrogen-bonded carbonyl band. We do not observe this, which simplifies the problem as we do not have to account for a decreasing concentration of methylol groups as the resol continues to polymerize upon the application of heat. Finally, the fraction of hydrogen-bonded carbonyl groups measured in the unheated resol-EVA[70] sample is very similar to that measured for the PVPh-EVA[70] blend at the same temperature (0.65 compared to 0.68, respectively). This instills confidence. To a first approximation, it

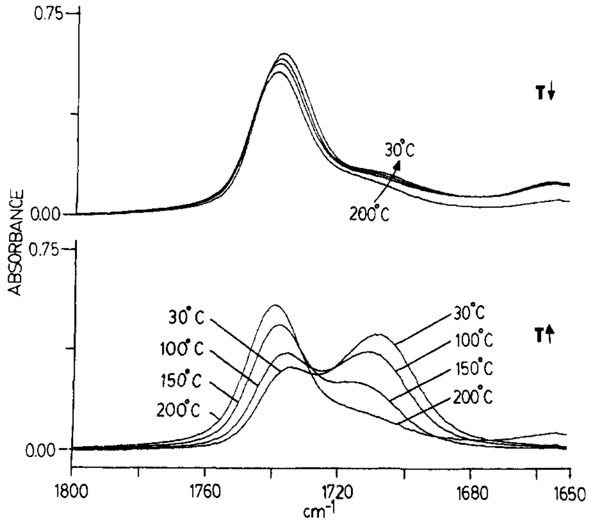

Figure 2. FTIR spectra of an 80:20 wt % resol-EVA[70] blend in the region from 1650 to 1800 cm^{-1}: (bottom) heating cycle; (top) cooling cycle.

Table III
Curve-Fitting Results for 80:20 Novolac–EVA[70] Blend

	"free" C=O			H-bonded C=O			
T, °C	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_F	ν, cm^{-1}	$W_{1/2}$, cm^{-1}	A_{HB}	fraction[a] H-bonded
			No Cross-Linking Agent				
30	1735	17	506	1705	31	2438	0.76
100↑	1735	18	571	1707	32	2272	0.73
150↑	1736	17	646	1710	33	2088	0.68
190↑	1737	17	680	1712	35	1808	0.64
150↓	1736	18	652	1710	34	1889	0.66
100↓	1736	18	594	1708	32	2040	0.70
30↓	1735	17	563	1706	33	2314	0.73
			With 5% Cross-Linking Agent				
30	1736	18	849	1706	33	2338	0.65
100↑	1737	19	986	1709	31	1952	0.57
150↑	1738	18	983	1712	34	1852	0.56
190	1739	19	1273	1716	42	1470	0.44
150↓	1739	19	1325	1714	42	1527	0.44
100↓	1738	19	1334	1712	42	1635	0.45
30↓	1738	19	1393	1709	42	1734	0.46

[a] As in Table I.

suggests that the differences in the chemistry of the structural units in PVPh and the PF resins are not very important to this study and supports the contention that the interaction between the phenolic hydroxyl group and the EVA[70] carbonyl group is dominant.

In contrast to the similarity between the results obtained for the unheated resol–EVA[70] and those for the room-temperature PVPh–EVA[70] blends, the differences between the two, as the samples are heated and subsequently cooled, are most striking. To reiterate, in the PVPh–EVA[70] system we found that we could cycle up and down within the temperature range studied and apparently obtain the equilibrium fraction of hydrogen-bonded carbonyl groups at any given temperature within the range. This is not true of the resol–EVA[70] blend system. As detailed in Table II, the fraction of hydrogen-bonded carbonyl groups decreases from 0.65 to 0.31 when the sample is heated from room temperature to 200 °C. The latter value is half that observed for the PVPh–EVA[70] blend at the same temperature (compare Tables I and II). Furthermore, although there is a perceptible increase in the fraction of hydrogen-bonded carbonyl groups as the sample is cooled to room temperature (0.31 to 0.35), most probably a simple consequence of the effect of temperature upon the equilibrium value, the initial room temperature value of 0.65 is never fully recovered. In other words, we appear to have lost about 50% of the original hydrogen-bonded intermolecular interactions between the resol and the EVA[70]. This is an important result and bears directly upon the effect of cross-linking upon the degree of molecular mixing. However, we will defer a discussion of the ramifications of this result until after we have described some additional experiments.

In Table II we have also included the results of curve fitting the carbonyl stretching region of three different samples of an 80:20 wt % resol–EVA[70] blend that were cured at 150 °C for different periods of time. The first sample was heated to 150 °C and the infrared spectrum recorded. It was then immediately quenched to room temperature, whereupon another spectrum was recorded. Essentially, full recovery of the fraction of hydrogen-bonded carbonyl groups was attained. For the other two samples, however, which were held for 5 and 30 min at 150 °C, respectively, the fraction of hydrogen-bonded carbonyl groups, measured both at 150 °C and after quenching to room temperature, decreased in a systematic manner. Only 57% of the carbonyls are hydrogen bonded at room temperature after the heat treatment for 30 min at 150 °C. This is an intermediate value between that observed for the PVPh–EVA[70] blend and that for the resol–EVA[70] system which had been cured at 200 °C. Again, we will defer discussion of the implication of these results until we have considered the experiments performed on the novolac blends.

Novolac–EVA[70] Blends. A novolac is a PF resin synthesized from a molar excess of phenol with formaldehyde (commonly 1.25:1) under acidic conditions.[15] Unlike resol resins, novolacs do not contain reactive methylol groups that are capable of undergoing cross-linking on heating. Rather, they are permanently fusible and may be viewed as representing a complete reaction product. Viewed simply, a typical novolac resin might be described as a complex mixture of polynuclear phenols linked by *o*- and *p*-methylene groups. In commercial materials the polymer chains are essentially linear (although some branching has been detected) and have average molecular weights of about 600. Curing a novolac requires a cross-linking agent such as hexamethylenetetramine (HMT) which yields a network that is, in the main, composed of phenolic rings joined together by methylene bridges with a minor amount of various nitrogen-containing links. Fortunately, as in the case of the heat-cured resol resins, the curing of a novolac with HMT does not materially alter the concentration of phenolic hydroxyl groups.

Figure 3 shows the carbonyl stretching region of the infrared spectrum for an 80:20 wt % blend of a novolac with EVA[70]. A film was cast from THF onto a KBr window, heated to 100 °C under vacuum for 3 h to eliminate the solvent, and cooled to room temperature prior to infrared analysis. In common with the experiments described above, spectra were recorded upon heating and cooling. A maximum temperature of 190 °C was used in this case, as it was determined independently that significant chemical changes occurred at 200 °C and above. The results of curve fitting the spectral data are given on Table III. Not surprisingly, there is a distinct similarity in the results and trends for the novolac–EVA[70] and PVPh–EVA[70] blend systems. Both samples can be cycled up and down in temperatures with little effect on the measured equilibrium fraction of hydrogen-bonded carbonyl groups determined for a particular temperature within the range studied.

What now happens if we add a cross-linking agent to the novolac–EVA[70] blend system and repeat the above ex-

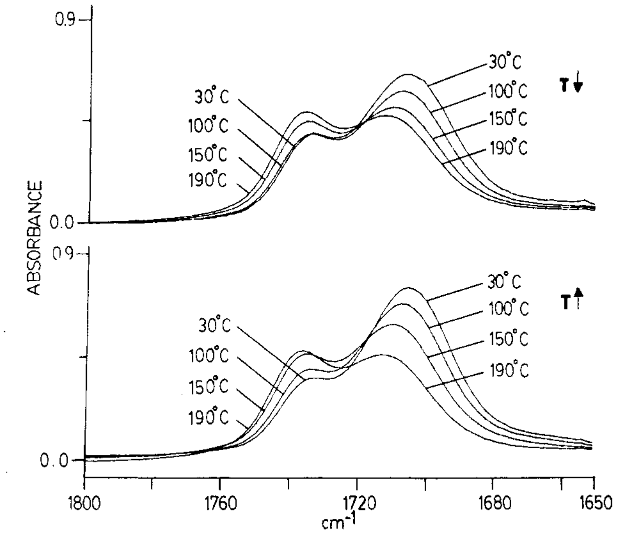

Figure 3. FTIR spectra of an 80:20 wt % novolac–EVA[70] blend in the region from 1650 to 1800 cm^{-1}: (bottom) heating cycle; (top) cooling cycle.

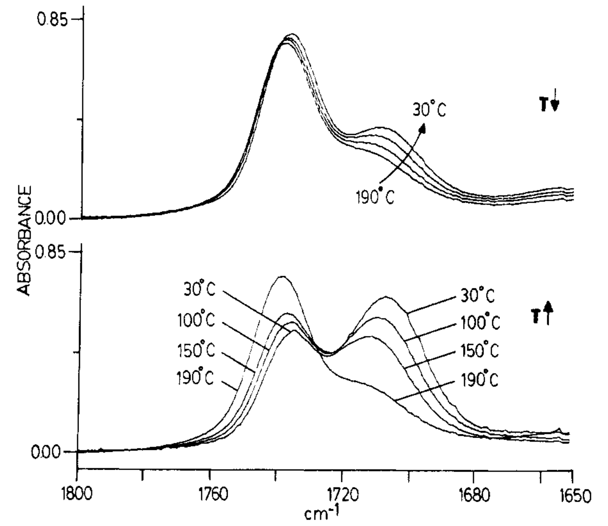

Figure 4. FTIR spectra of an 80:20 wt % novolac–EVA[70] blend containing HMT in the region from 1650 to 1800 cm^{-1}: (bottom) heating cycle; (top) cooling cycle.

periment? Before this question is addressed, we should first discuss how the sample was prepared. HMT is not readily soluble in THF, and it was necessary to change our film-casting method to accommodate the cross-linking agent. A common solvent mixture, DMF/MeOH (80:20 by volume), was used to dissolve the novolac, EVA[70], and HMT (5% of the weight of novolac). A film was cast from this solution onto a KBr window, and the solvent was removed by heating to 100 °C in a vacuum oven for 6 h. We cannot be entirely sure that some reaction with HMT did not take place during the removal of the solvent. HMT is known to react with phenols having free ortho and para positions at temperatures of 130–150 °C.[15]

Figure 4 shows infrared spectra in the carbonyl stretching region of the novolac–EVA[70] blend containing 5% HMT. Spectra recorded at 30, 100, 150, and 190 °C are shown during heating of the sample and at the same temperatures upon subsequent cooling. The contrast between Figures 3 and 4 (the novolac–EVA[70] system without and with a cross-linking agent) is again striking. Curve-fitting results of the spectra displayed in Figure 4 are listed in Table III. Comparing the initial results obtained at 30 °C, we see that the fraction of hydrogen-bonded carbonyl groups is less in the case of the blend containing the HMT (0.65 compared to 0.76). As mentioned above, this could indicate some reaction has occurred during the removal of the solvent. Another possibility is that a degree of phase separation occurred during the evaporation of the solvent ($\Delta\chi$ effect). In any event, we must not lose "the woods for the trees". The most important conclusion is that in the presence of HMT the fraction of hydrogen-bonded carbonyl groups in the novolac–EVA[70] system decreases significantly, above and beyond the equilibrium reduction expected from the increase in temperature, and is not recovered upon cooling to room temperature.

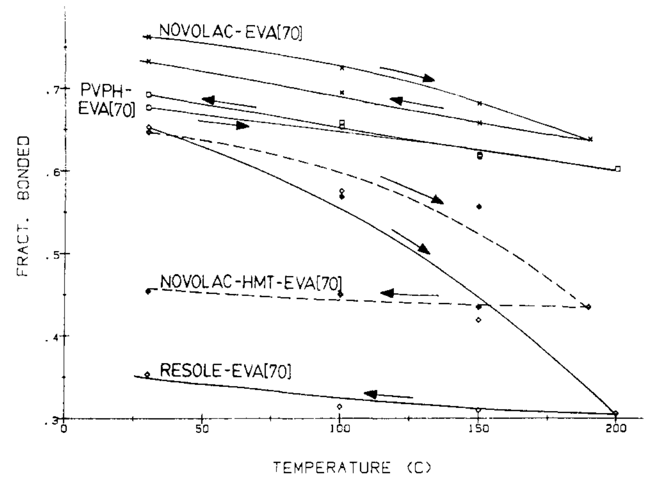

Figure 5. Plot of the fraction of hydrogen-bonded EVA[70] carbonyl groups in the different phenolic blends during the heating and cooling cycle.

Tentative Interpretation. Figure 5 summarizes, in graphical form, the major points we wish to emphasize. In essence, the PVPh–EVA[70] and novolac–EVA[70] blends appear to be homogeneous single-phase systems. It is our contention that intermolecular interactions in miscible polymer blends assume an equilibrium distribution.[5] The number of specific intermolecular interactions occurring between the different components is determined by the strength of the interaction, the blend composition, and the temperature. For the blends studied in this paper, hydrogen bonds between the phenolic hydroxyl and the EVA carbonyl groups are the dominant intermolecular interactions. The polymer mixture is in a dynamic state with the hydrogen bonds continuously formed and broken. Within the temperature range studied these blends may therefore be cycled up and down in temperature, and with favorable kinetics and in the absence of degradation, etc., the equilibrium number of intermolecular interactions will be formed at a given temperature. This is essentially what we observe in the novolac and PVPh blends with EVA[70]. We should note that there was no evidence for the existence of a lower critical solution temperature (LCST) up to 200 °C. It is unfortunate that degradation becomes significant above 200 °C and we have been unable to determine a LCST.

Returning to Figure 5, we see a most striking feature in the behavior of the novolac–HMT–EVA[70] and resol–EVA[70] blend systems. In both cases, they initially appear to be single-phase systems (at room temperature the fraction of hydrogen-bonded carbonyl groups is similar to that of the EVA[70] blends with novolac or PVPh). Upon heating, however, when the phenolic polymer increases in molecular weight, branches, and cross-links, the fraction of hydrogen-bonded carbonyl groups decreases above and beyond that anticipated from equilibrium temperature effects. On the other hand, the effect of temperature on the equilibrium concentration of hydrogen-bonded carbonyl groups is evoked to explain the measurable, albeit small, increase in the fraction of these groups as the sample is cooled to room temperature. Furthermore, and more importantly, the fraction of hydrogen-bonded carbonyl groups does not recover to, or closely approach, the initial value determined before heating. All in all, this strongly suggests partial phase separation.

In an attempt to rationalize the above observations, it is easy to become intimidated by the number of factors that could conceivably play a role. First we must question whether or not we can attain, or even approximate, equilibrium conditions. For example, if we wait long enough, would the fraction of hydrogen-bonded carbonyl groups in the resol–EVA[70] blend heated at 200 °C approach the original value measured at room temperature before the heat treatment? In other words, do we have a diffusion problem? We recognize that the T_g of the PF resin increases upon cross-linking and that it is possible that the system is frozen in the glassy state. Certainly, this would reduce mobility. At first glance one might tend to reject the lack of mobility argument because the blend was well mixed at the beginning. If lack of mobility is a factor preventing mixing, why would it also not prevent demixing? Alas, there is a further complication. It has been established that in single-phase polymer mixtures the LCST decreases significantly as the molecular weight of one or both of the components increases.[17] We do not know the LCSTs of the initially prepared solution-cast PF blends. The evidence suggests that in the case of the EVA[70] blends with PVPh and the uncured novolac any LCST is well in excess of 200 °C.[2]

In any event, the following scenario is possible. When the temperature is raised, the resol polymer (and the novolac in the presence of HMT) increases in average molecular weight, branches, and cross-links. While this is occurring, the hypothetical LCST is coming down. If the LCST falls below the experimental temperature, phase separation will occur, assuming sufficient mobility and favorable kinetics. Add to this an increasing T_g with curing, and it is not difficult to conceive of a LCST-driven phase-separated system that is frozen in place by a T_g greater than room temperature.

Although the above appears to be a reasonable rationalization, there are further factors that must be considered. The average molecular weight of the resol does indeed increase as the polymer undergoes the cross-linking reactions but so does the breadth of the distribution. At the incipient gel point, for example, there are infinite structures (gel) existing in concert with branched and linear structures of finite molecular weights (sol), ranging from the size of monomers to extremely large, but still finite, polymers. We might therefore anticipate a partial segregation to occur based upon a "fractionation" of molecular weights. This is not unlike de Gennes's description of the gelation process in the presence of a solvent.[18] In simple terms, the EVA[70] polymer prefers to associate with the lower end of the resol molecular weight distribution where there are more favorable entropic contributions to mixing. The upshot of such a fractionation is for segregation to occur into an essentially pure phenolic resin phase and a second mixed resol–EVA[70] phase. The latter now has a concentration of phenolic hydroxyl groups less than that of the original blend composition because a fraction of the phenolic resin has been removed. Accordingly, the equilibrium fraction of hydrogen-bonded carbonyl groups at any given temperature will reflect the decreased concentration of phenolic hydroxyl groups in the mixed phase. A crude estimate of the composition of this mixed phase can be obtained from the graph showing the fraction of hydrogen-bonded carbonyl groups as a function of composition for the single-phase PVPh–EVA[70] blend system (Figure 9 of ref 5). For example, a value of 0.35 (see Table II) implies a blend composition of about 40% by weight of the phenolic material. Finally, it should also be mentioned that there are definite parallels to the above in the studies of the PVPh–EVA[45] blend system, which is partially miscible and composed of an essentially pure PVPh phase and a mixture of the two polymers that is EVA[45] rich.[3] It should perhaps be mentioned that we have performed thermal analyses on the cross-linked PF resin blends. This was a frustrating exercise, however, from which no useful information was gained.

Concluding Remarks

In all candor, the results presented in this paper should only be used as signposts for future, more rigorous, experiments. Speculation is inevitable given the complexity of the systems studied. In our defense, we emphasize that our original intention was to attempt to significantly alter the physical properties of PF resins by incorporating a macromolecular plasticizer to the system by forming a miscible semi-IPN. Somewhere along the way we became sidetracked as we realized the ramifications of our results to the overall subject of the molecular mixing and interpenetration of polymers. The question of miscibility in IPNs has been addressed by Binder and Frisch,[19] but their theoretical treatment was limited to weakly cross-linked networks and weak interactions that could be represented by a Flory–Huggins interaction parameter. This study shows that at the scale size probed by vibrational spectroscopy even strongly interacting systems phase separate upon cross-linking. Questions that now come to mind include the following: Are "truly miscible" IPNs and semi-IPNs possible? Is microphase separation inevitable after a certain concentration of cross-links? What role does the gel fraction play? Is it possible to offset the drive toward phase separation by increasing the strength of the intermolecular interactions between the different polymers? We believe the stage is now set to use the infrared probe in carefully selected, and less complicated, polymer blend systems to answer such questions.

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Registry No. EVA (copolymer), 24937-78-8; HMT, 100-97-0; $(C_6H_5OH)(HCHO)$ (copolymer), 9003-35-4; poly(4-vinylphenol) (homopolymer), 24979-70-2.

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