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Compatibility of Polymer Mixtures Containing Novolac Resins

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ABSTRACT: Certain novolac resins were found to be compatible with poly(ethyl acrylate), poly(ethyl methacrylate), poly(methyl methacrylate), poly(vinyl acetate), poly(styrene-*co*-acrylonitrile), poly(2-methyl-1-pentene sulfone), polycarbonate, and poly(vinyl methyl ether). However, poly(4-vinylphenol) was found to be incompatible with poly(methyl methacrylate) or poly(styrene-*co*-acrylonitrile). Chemical interaction between the novolac resins and either poly(ethyl methacrylate), poly(ethyl acrylate), poly(vinyl acetate), poly(methyl methacrylate), or polycarbonate was manifested by a shift of $\sim 20\ \text{cm}^{-1}$ in the infrared stretching frequency of the carbonyl group. Large positive deviations of the experimentally observed glass transition temperatures from the calculated weight-average values were noted in mixtures containing poly(vinyl methyl ether) or poly(ethyl acrylate). The compatibility of these systems is discussed in terms of increased specific interactions between unlike polymers and decreased specific interactions between like polymers.

Introduction

Although novolac resins are used widely as ingredients in coatings and adhesives,[1] their miscibility with high molecular weight polymers has not been extensively documented.[2] We wish to report the results of a preliminary study in which the miscibilities of four novolac resins with polystyrene (PS), poly(styrene-*co*-acrylonitrile) (PSAN), poly(ethyl acrylate) (PEA), poly(vinyl acetate) (PVA), poly(ethyl methacrylate) (PEMA), poly(methyl methacrylate) (PMMA), poly(2-methyl-1-pentene sulfone) (PMPS), bisphenol-A polycarbonate, and poly(vinyl methyl ether) (PVME) were investigated by calorimetry.

In order to help to understand the reasons for the miscibilities, the specific polymer–polymer interactions were investigated by infrared (IR) spectroscopy. In contrast to previous IR studies on different polymer–polymer systems,[3-6] we observed interactions that gave relatively large shifts in the infrared stretching frequencies of the carbonyl groups.

Experimental Section

1. **Materials.** PS, PSAN containing 25% by weight of acrylonitrile, PVME, PEMA, and poly(4-vinylphenol) were purchased from Polysciences, Inc. PMMA and PEA were obtained from Cellomer Associates, Inc. PMPS, an alternating copolymer of 2-methyl-1-pentene and sulfur dioxide, was prepared in this laboratory by a procedure which has been reported previously.[7] Bisphenol-A polycarbonate was a stabilizer-free sample obtained through the courtesy of General Electric Co. PVA was supplied by Aldrich Chemical Co. All polymers were dried in a vacuum oven at 100 °C overnight prior to use.

The novolacs were made by condensing formaldehyde with mixtures of substituted phenols. The published method for unsubstituted novolacs[8] was modified by allowing the reaction to proceed for 18 h at reflux before water and unreacted phenols were removed by vacuum distillation. Novolac 1 was synthesized here, novolac 2 at Polychrome, and novolacs 5 and 8 at Mead Chemical Co. according to our specifications (see Table I).

The blend samples for calorimetric studies were prepared by mixing appropriate amounts of the constituents in 2-butanone and allowing the solvent to evaporate slowly at room temperature. In the case of the polycarbonate mixture, methylene chloride was used as the solvent and the temperature of solvent evaporation was maintained at about 45 °C to increase the solubility of the novolac resin. The samples were again vacuum dried at 100 °C overnight.

Infrared studies were made by casting films from solution on salt plates, using concentrations adjusted to give about 20% transmittance through the dried film in the region of interest. The solvent was a mixture of 10% tetrahydrofuran–90% methylene chloride. The concentrations were as follows:

Blends for IR Studies

studies on carbonyl region	studies on hydroxyl region
95% novolac	2–4% novolac
5% carbonyl compound	98–96% carbonyl compound

The solvent was allowed to evaporate at room temperature followed by vacuum drying for 2–5 h at 85 °C. In one case when the film was used without this final drying the wavelengths absorbed were the same but the spectrum was not as well resolved.

2. **Calorimetry.** A Du Pont Model 990 differential scanning calorimeter was used for glass transition temperature measurements. The transition temperature was taken as the onset (extrapolated) of the abrupt increase in the specific heat of the specimen. Specimens were first heated at 10 °C/min to 100 °C in the calorimeter and then quenched by liquid nitrogen to an appropriately low temperature, after which heating was resumed. The experiment was repeated at least twice for each specimen and the reproducibility of the T_g value was about ±0.7 °C unless otherwise stated.

3. **Infrared Spectroscopy.** A Perkin-Elmer Model 597 infrared spectrometer was used for the IR studies. One sample was checked on a Digilab Fourier transform infrared spectrometer but gave qualitatively the same spectrum. All spectra were run on salt plates. To check that the shifts were not caused by changes in the index of refraction of the different polymers, a polished silicone plate was also used as the substrate in one experiment.[9] No difference in the wavelength of absorption was observed whether salt or silicone was used.

Results

Novolac 1 was incompatible with PS. The mixture was cloudy and two distinct T_g's were found in the thermogram. All the mixtures listed in Table II were compatible with each mixture, showing one T_g, which, except in the case of novolac 1 with PVME and with PEA, was either equal to or lower than the calculated weight-average value

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Table I
Novolacs Used in Study

novolac source	mol % phenols in feed: *p-tert*-butyl	*2-tert*-butyl	*m*-cresol	*o*-cresol	mol % formaldehyde in feed	max temp of dist, °C	% free phenol in polymers[a]	$\overline{M}_n$[b]	polystyrene equiv $\overline{M}_n$[c]
1	13		17	70	95	160	3	780	1160
2	13		17	70	95	160	3	800	1400
5		15		85	130	220		1600	
8		15	17	68	95	220		1200	1600

[a] By gas chromatographic analysis. [b] By vapor phase osmometry. [c] By gel permeation chromatography after vacuum drying to remove residual free phenols.

Table II
Glass Transition Temperatures

	material	wt % novolac	T_g, °C
A.	novolac 1	100	46
	poly(ethyl methacrylate)	0	63
		50	50
	poly(2-methyl-1-pentene sulfone)	0	88
		50	50
	poly(methyl methacrylate)	0	105
		50	58 ± 2
	poly(styrene-*co*-acrylonitrile)	0	105
		50	60
	polycarbonate	0	146
		80	61
	poly(vinyl methyl ether)	0	−31
		21	−16
		36.3	−3
		51.3	18
		61	32
		71	35
		81	42
	poly(ethyl acrylate)	0	−24
		80	40
		65	33
		50	21
		35	3
		20	−9
	novolac 5	0	96
		50	61
B.	novolac 2	100	52
	poly(2-methyl-1-pentene sulfone)	91	56
		50	62
C.	novolac 8	100	74
	poly(ethyl acrylate)	0	−24
		50	26
	poly(vinyl acetate)	0	26
		91	66
		9	30
	poly(2-methyl-1-pentene sulfone)	50	76
	poly(methyl methacrylate)	50	76
		50	87

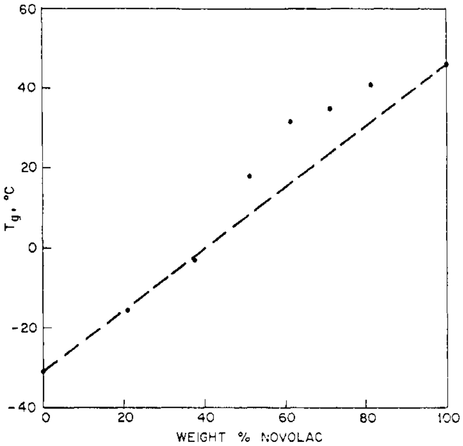

Figure 1. T_g vs. wt % novolac for PVME + novolac 1.

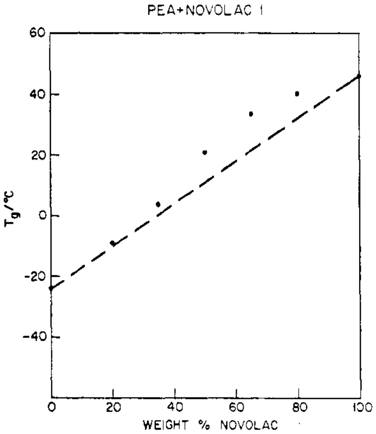

Figure 2. T_g vs. wt % novolac for PEA + novolac 1.

Table III
Carbonyl Infrared Frequencies (cm^{-1})

material	wt % novolac	major carbonyl freq
poly(ethyl methacrylate)	0	1720
	95	1700
poly(methyl methacrylate)	0	1722
	95	1705
poly(vinyl acetate)	0	1735
	95	1715
polycarbonate	0	1770
	95	1750
poly(ethyl acrylate)	0	1729
	95	1710

(Table II). Poly(4-vinylphenol) was incompatible with either PSAN or PMMA.

The T_g data for blends of novolac 1 with PVME are plotted in Figure 1. When the weight percentage of the novolac is 38% or less, the experimentally observed T_g values coincide with the weight-average values. At higher novolac concentrations the T_g results are substantially higher than the weight-average values. The magnitude of the ΔC_p indicated that the entire mass of the specimen was accounted for in each case. The largest deviations, about 13 °C, occur between 60 and 70 wt % novolac or approximately 46–57 mol (segmental) %. Similar results for blends of novolac 1 with PEA are shown in Figure 2. The largest deviation of the experimental T_g data from the weight-average values occurs at 60–65 wt % novolac or 56–60% mol %. These positive deviations from the weight-average values are very unusual and, to our knowledge, have been found for only a few other pairs of amorphous, nonionic polymers, namely, poly(styrene-*co*-(vinylphenyl)bis(trifluoromethyl)carbinol) mixed with poly(butyl methacrylate) or polycarbonate[10a] and poly(vinyl nitrate) mixed with poly(vinyl acetate).[10b]

The infrared carbonyl stretching frequency of the various polyesters and polycarbonate is shifted to lower

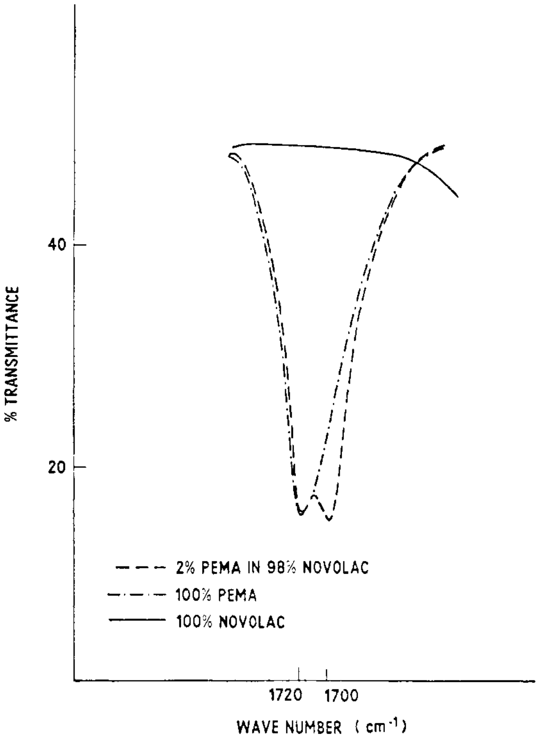

Figure 3. Infrared carbonyl stretching region for 2% PEMA in 98% novolac, 100% PEMA, and 100% novolac.

wavenumbers by 17–20 cm^{-1} in the presence of novolacs (Table III). Only part of the carbonyl band is shifted for some of the polyesters since the peak is split to form a doublet with some of the absorption remaining at the higher frequency; a substantial absorption, however, is now at the lower frequency (Figure 3). The remaining portion is not hydrogen bonded for conformational reasons. In the polycarbonate case, on the other hand, the entire carbonyl peak is shifted 20 cm^{-1}, with no portion remaining at the higher value (Figure 4). No obvious change in the PMPS absorption could be observed in the presence of the novolacs.[11]

The frequency of the absorption band of the hydroxyl group of the novolacs is changed considerably by mixing with the carbonyl compounds. Instead of a broad peak stretching from 3600 to 3100 cm^{-1}, a single or multiple peak which is considerably sharpened from that in the pure novolac is observed. This sharpening effect was also observed with a film of the novolac PMPS mixture (Table IV).

To check if hydrogen bonding is involved in the PMPS case, we also studied this system in dilute solution in an inert solvent, benzene. Since the novolacs themselves are not soluble in benzene or in any inert solvent tried, the model compound *m*-cresol was used. The *m*-cresol had a single absorption at 3525 cm^{-1}, which was supplemented by an absorption at 3470 cm^{-1} in the presence of PMPS, presumably due to hydrogen bonding between the *m*-cresol and the PMPS.

Discussion

The reasons that these novolacs are compatible with such a wide range of polymers are probably threefold: the moderate molecular weight of the novolacs, hydrogen bonding between polymer pairs, and matching of polarities between the polymers.

The moderate molecular weight of the novolac resins (800–1600) favors miscibility, as the relationship between molecular weight and critical miscibility parameters is well-known.[2,12] But the low molecular weight is not a sufficient reason for miscibility with the large number of polymers studied here because the novolac resins are not compatible with PS, a nonpolar polymer. The chemical structures of the polymers, therefore, must play a dominant role.

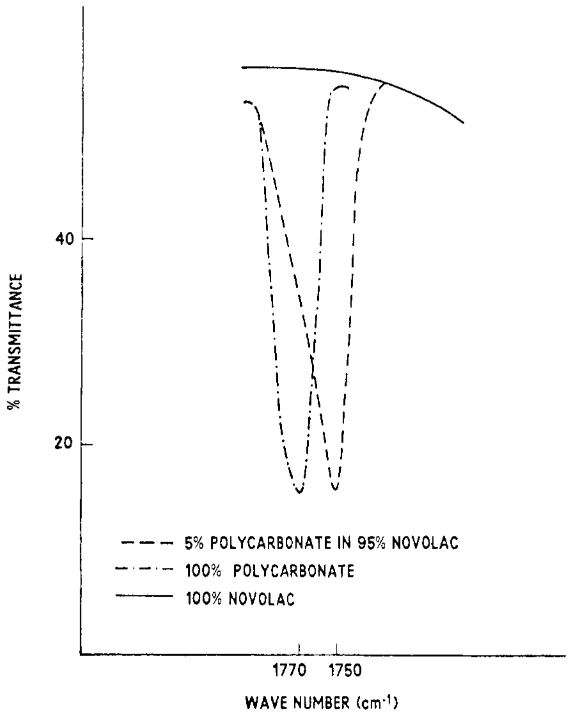

Figure 4. Infrared carbonyl stretching region for 5% polycarbonate, 100% polycarbonate, and 100% novolac.

Table IV
Hydroxyl Infrared Frequencies (cm^{-1})[a]

material	wt % novolac	hydroxyl freq
novolac 8	100	3100-3600
novolac 1	100	3100-3600
PEMA	4	3420
bisphenol-A polycarbonate	2	3520 s, 3660 w
PEA	4	3450 s, 3550 sh, 3620 w
PMPS	2	3500 s, 3610 w
1% *m*-cresol in benzene		3525
1% *m*-cresol + 10% PMPS in benzene		3525 s, 3470 m

[a] s = strong, m = medium, w = weak.

Since the driving force for polymer miscibility comes largely from a favorable heat of mixing, it may be worthwhile to reexamine the familiar expression $\Delta\epsilon$ for the change in pair contact energy

$$\Delta\epsilon = \frac{1}{2}(\epsilon_{11} + \epsilon_{22}) - \epsilon_{12} \qquad (1)$$

when the ϵ's are the energies of contact dissociation between like and unlike species. The concepts of specific interaction and complementary dissimilarity[13] focus on the term ϵ_{12}. It is obvious from eq 1 that an appropriate change in ϵ_{11} or ϵ_{22} can also lead to a favorable value of $\Delta\epsilon$.

In other words, two ways of promoting compatibility are (1) increasing interaction between unlike species (such as hydrogen bonding between novolac and carbonyl groups) and (2) decreasing interaction between like species (such as decreased hydrogen bonding between novolac and novolac).

The hydrogen-bonding interaction between novolac and carbonyl are seen by the IR shifts (see Table III), which show that strong hydrogen bonding occurs between the phenolic hydrogen and the carbonyl oxygen of the polycarbonate or the polyester polymers. The reason the entire carbonyl peak is shifted in the polycarbonate but not in the other cases is that the stringent geometric requirement for hydrogen bonding is more easily met in the relatively unhindered carbonate functional group. There should also be hydrogen bonding between the novolac and the ether oxygen of PVME but the alcohol end groups of the PVME interfered with direct interpretation of the IR. Hydrogen bonding between phenols and esters, carbonates, or ethers has been extensively documented in monomeric compounds.[14]

In the polysulfone case hydrogen bonding should be much weaker, although it has been reported that the OH frequency shift for the association of *p*-chlorophenol with diethyl sulfone is 176 cm^{-1}.[15] We found an OH frequency shift of 55 cm^{-1} for *m*-cresol with the PMPS (Table IV). However, we did not find any shift in the sulfone absorption.[11] The polysulfone–novolac interaction and, therefore, compatibility in that system are marginal. Changing to poly(1-butene sulfone) from PMPS is enough to cause the system to become incompatible.

Hydrogen bonding is also the reason that adding acrylonitrile units to polystyrene to form PSAN results in compatibility with the novolacs. In small molecules, shifts of 150–200 cm^{-1} have been obtained as a result of nitrile–phenol interaction.[16,17] The compatibility results through the interaction ϵ_{12} between the hydroxyl and the nitrile groups, although ϵ_{22} must have also increased to some extent. Some polymeric phenols, such as poly(4-vinylphenol), are incompatible with PSAN or PMMA but our substituted-phenol novolacs are compatible. The regular geometry of poly(4-vinylphenol) allows it to form hydrogen bonds with itself more readily than do the novolacs. Since the novolacs are more polar than the second constituent in the mixture, any chemical modification which would decrease the novolac polarity would decrease the energy of dissociation of a novolac–novolac contact, ϵ_{11}, by a substantial amount and thereby result in a favorable $\Delta\epsilon$. This simple approach does not appear to be fully appreciated in previous studies of polymer compatibility.

That there is decreased hydrogen bonding between novolac and novolac in the compatible mixtures was suggested by the sharpening of the bands in the OH frequency region and the shift to higher frequency as compared with those of the pure novolac (Table IV).

Increasing the polarity of PS and decreasing the polarity of the phenol allow the proper balance between ϵ_{12} and ϵ_{22}.

The anomalous positive deviations of the T_g's with PVME and PEA are very likely due to a favorable packing of the chains as a consequence of hydrogen bonding. The bonds act as "cross-links" in the system. We recall that the geometric fitting of syndiotactic and isotactic PMMA chains can result in the formation of 2:1 or 1:1 "complexes".[18-20] Although the reason for the intertwinement of chains in our systems is probably due to a hydrogen-bonded complex, rather than to geometric fitting, we are nevertheless fascinated by the observation that the maximum T_g deviation occurs at blend compositions containing approximately 50 mol % novolac.

The evidence for a hydrogen-bonded complex is strengthened by the fact that the only other systems which we know to give positive deviations of T_g are also made up of acidic polymers mixed with polymers that would tend to accept hydrogen bonds.[10]

We also note that flexible chains such as PVME and PEA produce the high T_g effects. The anomalously high T_g's we find when small amounts of PVME and PEA flexible polymers are dissolved in a rigid novolac seem similar to us to the antiplasticizer effect of small amounts of plasticizer in rigid polymers.[21]

Conclusion

We have observed that certain substituted novolac resins are compatible with a wide range of polymers. The latter are characterized by the capability of forming hydrogen bonds with the novolac as evidenced by shifts in the IR spectra of many of these polymers. We also believe that it is important to "match" polarities of polymers in order to have compatible mixtures. Even polymers containing groups which have a high tendency to form hydrogen bonds, such as polyphenols and polymethacrylates, will not be compatible unless modified so that the interaction between unlike molecules becomes more favorable than the interaction between like molecules. Modifying the novolacs with alkyl substituents and modifying PS with acrylonitrile are examples of this polarity control which results in compatible mixtures.

In addition we have observed large positive deviations of the experimentally observed glass transition temperatures from the calculated weight-average values in hydrogen-bonded novolac–PVME mxitures and novolac–PEA mixtures.

Acknowledgment. We thank M. Y. Hellman for the molecular weight determinations of the novolacs, C. A. Pryde for the FT IR spectrum and for information about the polycarbonate sample, E. M. Doerries for providing the PMPS sample, and M. J. S. Bowden and D. L. Allara for their encouragement.

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