

Hydrogen-Bonded Polymer Blends. Blends Containing Poly(4-hydroxystyrene-co-4-methoxystyrene) Copolymers

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ABSTRACT: The miscibility between partially methoxylated poly(4-hydroxystyrene) with poly(vinyl acetate), poly(methyl acrylate), and poly(ethyl acrylate) was assessed based on glass transition temperature over the entire composition range. Quantitative analyses of the fraction of hydrogen bonded carbonyl groups were made by FT-IR spectroscopy for all systems. Good correlation between thermal behavior and infrared results was observed. The results are discussed considering the influence of two factors on miscibility, decrease of $-\text{OH}\cdots\text{C}=\text{O}$ hydrogen bonds in the blend and autoassociation as a function of methoxylation degree.

KEY WORDS Blends / Miscibility / Hydrogen Bonds / Autoassociation / Glass Transition / FT-IR Spectroscopy /

From thermodynamic considerations that, in general, polymer pairs are immiscible,^{1,2} miscibility being most frequently associated with specific interactions,³ among which hydrogen bonds are probably the most important ones.^{4,5} In recent years a significant amount of work has been devoted to the characterization of these polymer blends.⁶⁻¹⁰

Due to the wide range of experimental conditions (temperature, pressure, presence of solvent, etc.) in technological processes, it is necessary to have a theoretical framework that allows one to calculate the phase diagram and relevant thermophysical properties of the blends under such conditions. The existence of hydrogen bonds possesses strong difficulties for building-up such a theory, and in spite of the encouraging results of some recent mod-

els,¹¹⁻¹⁴ the problem is still far from being solved and further systematic experimental research is needed.

In previous papers¹⁵⁻¹⁸ we focused on blends containing poly(4-hydroxystyrene) (P4HS) as a polymer that can form both intra- and intermolecular hydrogen bonds due to the existence of one $-\text{OH}$ group in each repeating unit. We used poly(vinyl acetate) and poly(*n*-alkylacrylate)s to form the blends since they contain carbonyl groups that can act as proton acceptors in the blends.

Most of the theoretical models¹¹⁻¹³ include as one of the key variables the number of hydrogen-bonds, both in the homopolymers and in mixture. Therefore information on blends in which the capability of one or both homopolymers to form hydrogen bonds can be

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very useful to carry out a rigorous test of a theoretical model. P4HS can be modified by substituting some the hydroxyl groups by methoxy ($-\text{O}-\text{CH}_3$) ones,¹⁹ thus reducing its capacity to form hydrogen bonds.

In this paper we study blends of partially methoxylated P4HS with poly(vinyl acetate) (PVA), poly(methyl acrylate) (PMA), and poly(ethyl acrylate) (PEA). Besides the original P4HS homopolymer, four different samples of poly(4-hydroxystyrene-*co*-4-methoxystyrene) were used, so that the ratio ($-\text{OCH}_3/-\text{OH}$) covers the ratio 0 to 70%. FT-IR measurements were carried out to estimate the fraction of $-\text{OH}$ groups involved in hydrogen bonds following the procedure of Serman *et al.*²⁰ for P4HS + poly(*n*-alkylacrylate)s. In addition, DSC was used to study the composition dependence of the glass transition temperature of the blends. From the results, the influence of intra- and intermolecular hydrogen bonds upon the miscibility of the systems are discussed.

EXPERIMENTAL

Polymers

Poly(4-hydroxystyrene) (P4HS), poly(vinyl acetate) (PVA), poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), and poly(4-methoxystyrene) (PMEOX) were purchased from Polyscience (UK).

Polymer Characterization

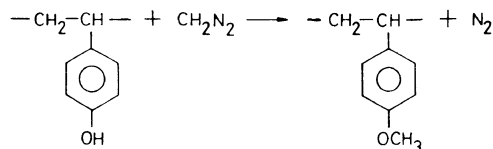
The weight average molecular weight, $M_w = 2 \times 10^5$ of PVA was determined at $T = 298$ K by light scattering using a Laser Dawn-F model from Wyatt Technology. The incident light was 488 nm and solutions of PVA in acetone with polymer concentration $c < 1.7 \times 10^{-3} \text{ g cm}^{-3}$ were used. The same polymer solutions measured in light scattering were used to determine $dn/dc = 0.104$ (n is the refractive index). The polydispersity index of this sample of PVA was determined by GPC in tetrahydrofuran (THF) solutions with a Waters 510

instrument, leading to $M_w/M_n = 2$. The viscosity average molecular weights, M_v , for PMA and PEA were $M_v = 1.1 \times 10^5$ and $M_v = 6.8 \times 10^5$, respectively. To obtain M_v from intrinsic viscosity, Mark-Howink equations in ref 21 were used.

The number average molecular weight $M_n = 5100$ of P4HS was determined at 318 K in THF solutions using a Knauer vapour pressure osmometer. The polydispersity index, $M_w/M_n = 2$, was obtained with the same instrument and under the same conditions as above.

Hydroxyl groups of P4HS may be oxidized to quinone ones,²² however both FT-IR and ^1H and ^{13}C NMR spectra showed that the number of quinonic groups was almost negligible.

The different samples of poly(4-hydroxystyrene-*co*-4-methoxystyrene) (PH-*co*-MS) were prepared from P4HS by reactions involving the phenolic hydroxyl group and diazomethane as shown schematically below.



Modified P4HS was prepared between 37% and 67% conversion, and chemical compositions determined by ^1H NMR. Table I lists the polymers used and also the T_g and abbreviated names for each polymer used here-after.

Solvents

The blends were prepared by solution casting with acetone (Ac) as solvent. Ac was Carlo Erba (RPE type).

Preparation of the Blends

The blends were prepared by casting 3% (w/v) solutions of the pure components in Ac. First, the solution was left until most of the solvent was evaporated. In the second step, the

Table I. Polymers used, abbreviated names and T_g

Polymer	Abbreviated name	T_g /K
Poly(vinyl acetate)	PVA	317
Poly(methyl acrylate)	PMA	291
Poly(ethyl acrylate)	PEA	262
Poly(4-hydroxystyrene)	P4HS	434
Poly(4-hydroxystyrene (63) ^a - <i>co</i> -4-methoxystyrene (37) ^a)	HSMS37	389
Poly(4-hydroxystyrene (48)- <i>co</i> -4-methoxystyrene (52))	HSMS52	385
Poly(4-hydroxystyrene (40)- <i>co</i> -4-methoxystyrene (60))	HSMS40	379
Poly(4-hydroxystyrene (33)- <i>co</i> -4-methoxystyrene (67))	HSMS67	373
Poly(4-methoxystyrene)	PMEOX	367

^a The figures in brackets show the percentage of 4-hydroxystyrene and 4-methoxystyrene in the modified polymers.

sample was kept in a vacuum and at ambient temperature for five days, and at 333 K ten more days, clear films were obtained for all the compositions.

FT-IR Measurements

FT-IR spectra were obtained using a Galaxy model apparatus from Mattson at 2 cm^{-1} resolution in the transmission mode. At least 32 scans were averaged for each spectrum. The films of the blends were cast directly onto KBr windows from solutions of concentrations below 1% in weight; Care was taken to keep the films thin enough for the Lambert–Beer law to be valid. The solvent was eliminated from the films according to the procedure described above.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out in a Perkin-Elmer DSC-4, over range 223 K to 473 K. In all the cases, the heating rate was 20° min^{-1} . Open aluminium pans were used with a sample weight ranging from 5 to 10 mg; measurements were made under N_2 atmosphere and subambient temperatures were reached using liquid N_2 to cool the DSC cell. The temperature scale was established using the indium melting-point as reference. T_g was taken from third scan at the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated

liquid and glassy base lines.

RESULTS

Figure 1 shows the spectra of the two homopolymers, P4HS and PMEOX, as well as those of the different copolymers in two regions, between 2700 and 3700 cm^{-1} and between 700 and 1900 cm^{-1} . In the high frequency region it is possible to observe the hydroxyl stretching vibration. The very broad band between 3100 and 3500 cm^{-1} was attributed to self associated hydroxyl groups⁶; the width of this band reflects the broad distribution that characterizes hydrogen bonding. A shoulder appears at 3525 cm^{-1} . Previous studies⁶ in P4HS, carried out as a function of the temperature, attribute the absorbance at this frequency to the free (non-hydrogen bonded) hydroxyls groups. As expected, this band does not appear in PMEOX, however even for highly methoxylated P4HS the band at 3400 cm^{-1} is very intense. This indicates that there still is a strong tendency of $-\text{OH}$ groups to hydrogen bond with other $-\text{OH}$ groups, either from the same polymer chain or from others (here-after, autoassociation).

Coleman *et al.*⁶ attributed the bands at 825 , 1110 , 1170 , and 1400 cm^{-1} and the doublet at 1595 – 1610 cm^{-1} to the aromatic ring of P4HS. The broad bands in the 1200 – 1400 cm^{-1} region are attributed to $-\text{OH}$ deforma-

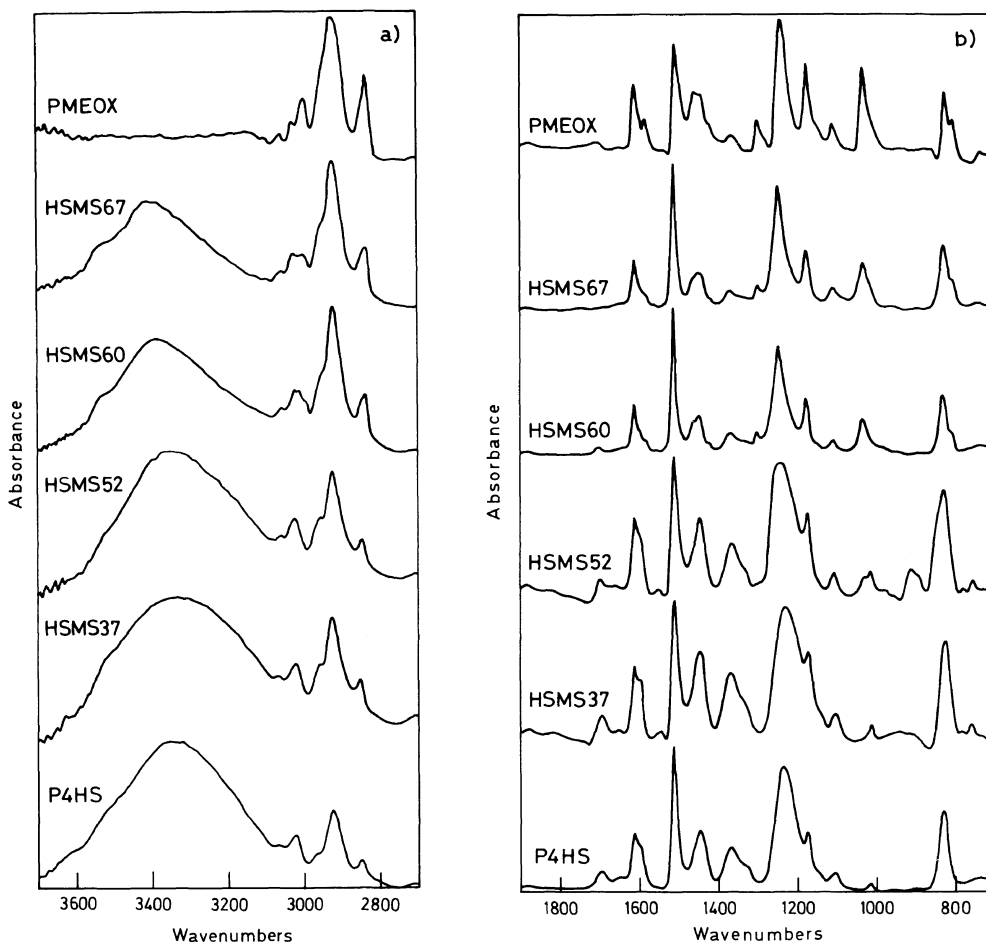


Figure 1. FT-IR spectra of P4HS, PMEOX, and copolymers. a) Infrared region between 2700 and 3700 cm^{-1} corresponding to hydroxyl stretching region. Bands at 3525 cm^{-1} and 3360 cm^{-1} are attributed to non-hydrogen bonded and hydrogen bonded hydroxyl groups, respectively. b) Infrared region between 700 and 1900 cm^{-1} .

tion and CO stretching. Figure 1b clearly shows the effects of the substitution of $-\text{OH}$ groups by $-\text{OCH}_3$ ones. The band at 825 cm^{-1} becomes a doublet and a band characteristic of PMEOX appears at 1041 cm^{-1} ; this band is assigned to the symmetric stretching of the ether group when it is connected to an aromatic ring. The band at 1613 cm^{-1} changes to a triplet at the highest modification level.

We studied room-temperature FT-IR spectra obtained from blend films of 0.5 weight fraction. Figure 2 shows the spectra in carbonyl stretching region (1800–1650 cm^{-1}) for blends

of P4HS or copolymers with PMA, PEA, and PVA. The carbonyl stretching vibration of PMA, PEA, and PVA occurs at 1735 cm^{-1} . Upon blending an additional band at 1710 cm^{-1} appears as a shoulder in the low frequency wing of the band and may be readily attributed to the stretching vibration of hydrogen-bonded carbonyl groups, *i.e.*, $\text{C}=\text{O}\cdots\text{HO}-\text{C}_6\text{H}_4-$. The shoulder at 1710 cm^{-1} confirms the miscibility at the molecular level and decreases as a function of increasing methoxy content in the modified polymers. Figure 3 shows FT-IR spectra in the hydroxyl

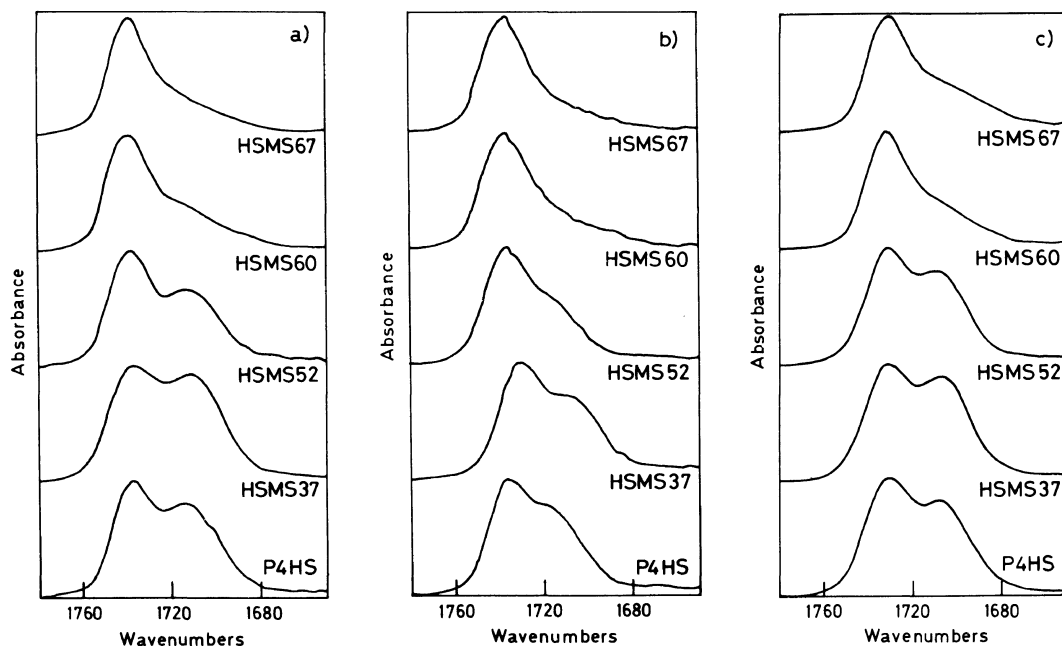


Figure 2. FT-IR spectra in the region of $1780\text{--}1650\text{ cm}^{-1}$ of blends of P4HS and copolymers with a) PVA, b) PMA, and c) PEA.

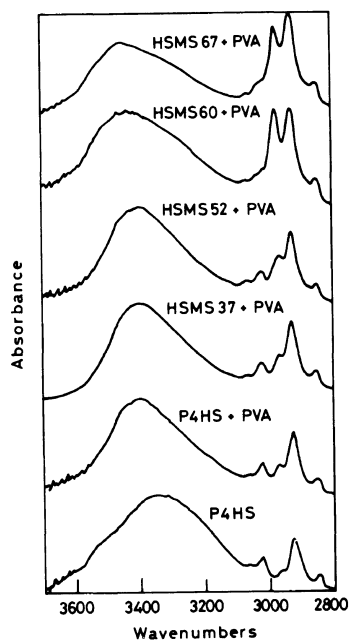


Figure 3. FT-IR spectra in the region $3700\text{--}2800\text{ cm}^{-1}$ of blends of P4HS and copolymers with PVA. For comparison, the FT-IR spectrum of pure P4HS is shown at the bottom.

stretching ($3800\text{--}2800\text{ cm}^{-1}$) for blends with PVA. This figure can be compared with Figure 1a corresponding to the homopolymer P4HS and copolymers. In general, the shape of the band is different when P4HS or copolymers are blended with PVA. In particular, the shoulder at 3525 cm^{-1} is not detected in the blends and only a band centered at $3400\text{--}3440\text{ cm}^{-1}$ assigned to --OH groups hydrogen bonded, remains. Similar behaviour is observed for other systems.

To make a more quantitative discussion we calculated the frequency corresponding to the maxima of the bands for free and associated carbonyl groups, ν^{assoc} and ν^{free} respectively. We obtained the percentage of hydrogen bonded carbonyls for each system. This information is summarized in Table II.

The shape of infrared absorption curves is often represented by Gaussian and Lorentzian curves. The second derivative of this kind of curves is a negative peak with two positive lobes. ν^{assoc} and ν^{free} were obtained through a

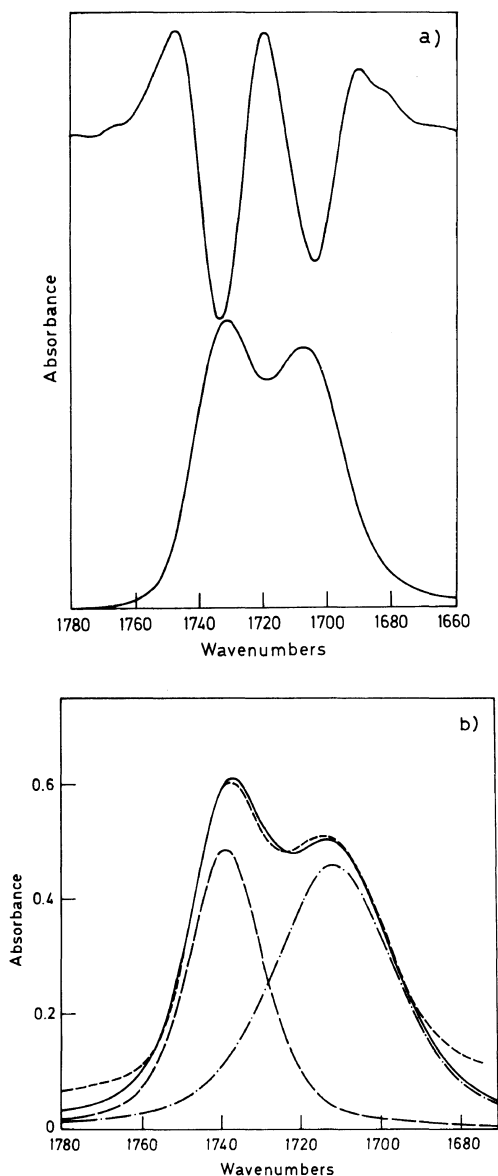


Figure 4. a) Second derivative spectrum for HSMS37 + PEA in the carbonyl region b) Experimental spectrum (----) compared with the spectrum (—) and components (— · —) (— · —) calculated by curve fitting for P4HS + PVA blend.

second derivative analysis in the carbonyl spectral region.²⁴ In Figure 4a we can see the second derivative spectrum for a representative blend HSMS37 + PEA in the carbonyl region. Two well-resolved negative peaks are observed

indicating the exact location of two bands at 1703 cm^{-1} corresponding to hydrogen-bonded carbonyl groups and at 1734 cm^{-1} corresponding to free carbonyl groups. The fraction of hydrogen bonded carbonyls was obtained, by curve fitting techniques,²⁵ to calculate the areas of the 1735 cm^{-1} and 1710 cm^{-1} bands in all spectra. The ratio of absorptivities $a_1/a_2 = 1.5$ (a_1 and a_2 correspond to associated and free carbonyl groups, respectively) was used.⁶ Figure 4b gives an example of the closeness of the fits.

The results of the fraction of H-bonded carbonyl groups for P4HS + PVA, P4HS + PEA, P4HS + PMA are in concordance with those obtained by Coleman *et al.*²³ for the same blends.

Figures 5 to 7 show the glass transition temperatures T_g for different blends through the whole composition range. In all cases there is a unique value of T_g for each composition, most frequently interpreted as miscibility of the blends. This is consistent with the FT-IR results that clearly show the existence of $-\text{OH}\cdots\text{C}=\text{O}$ hydrogen bonds in the mixtures. For blends with methoxylated P4HS, the experimental values of T_g are always below those calculated from the additivity rule:

$$T_{gAD} = w_1 T_{g1} + w_2 T_{g2} \quad (1)$$

where $w_1 = 1 - w_2$ is the weight fraction of the modified P4HS. This behaviour is in contrast with that of P4HS + PMA, P4HS + PEA, and P4HS + PVA¹⁸ for which T_g are closer to the additivity values mainly for rich P4HS compositions ($w_2 < 0.5$).

DISCUSSION

Figure 8 shows the values of the fraction of hydrogen bonded carbonyl groups (see Table II) as a function of the degree of methoxylation of P4HS for the blends. In general, this fraction decreases with increasing methoxylation of P4HS. This is in fact a negative contribution to miscibility, since it represents a reduction in

Table II. Values of the frequency, in cm^{-1} , corresponding to the maxima of the bands for free ν^{free} , and associated, ν^{assoc} , carbonyl groups and difference between them, $\Delta\nu$, for the system

Blends ($w_2=0.5$)	ν^{free}	ν^{assoc}	$\Delta\nu$	H-bonded carbonyl groups	
	cm^{-1}	cm^{-1}	cm^{-1}	%	
P4HS + PMA	1738	1711	27	39	(40) ^a
P4HS + PEA	1735	1704	31	42	(41) ^a
P4HS + PVA	1740	1711	29	47	(43) ^a
HSMS37 + PMA	1732	1704	28	39	
HSMS37 + PEA	1734	1703	31	46	
HSMS37 + PVA	1742	1709	33	43	
HSMS52 + PMA	1739	1711	28	31	
HSMS52 + PEA	1734	1705	29	37	
HSMS52 + PVA	1741	1710	31	35	
HSMS60 + PMA	1738	1709	29	18	
HSMS60 + PEA	1734	1707	27	28	
HSMS60 + PVA	1741	1711	30	30	
HSMS67 + PMA	1738	—	—	13	
HSMS67 + PEA	1734	1707	27	29	
HSMS67 + PVA	1740	1712	28	25	

^a from ref 23.

Last column shows the percentage of hydrogen bonded carbonyl groups calculated for each system.

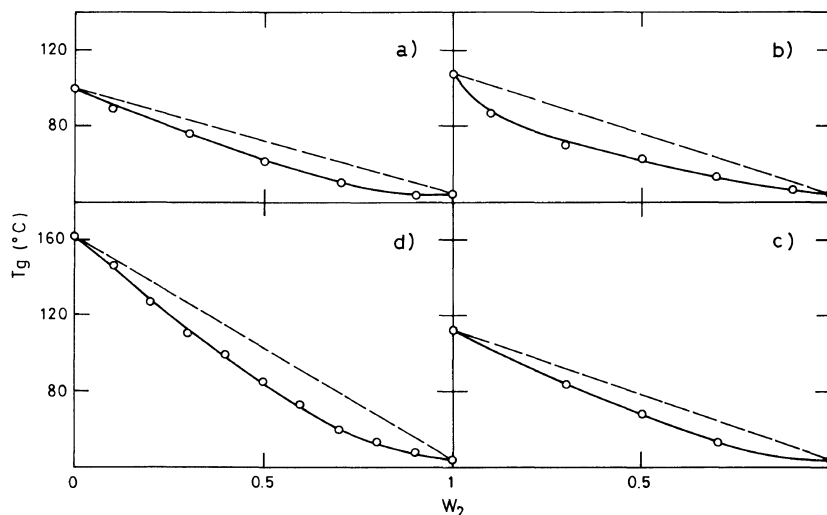


Figure 5. T_g as a function of the weight fraction of PVA in the blend, w_2 . a) HSMS67+PVA, b) HSMS60+PVA, c) HSMS52+PVA, and d) P4HS+PVA.¹⁸

the number of favourable interactions between the two polymers of the blends. There is another factor that must be considered; in effect, the tendency to autoassociate should be

modified as the P4HS is methoxylated. A decrease in $-\text{OH} \cdots \text{OH}$ hydrogen-bonds formation would result in a favourable contribution to miscibility. To evaluate this effect, Table

Hydrogen-Bonded Polymer Blends

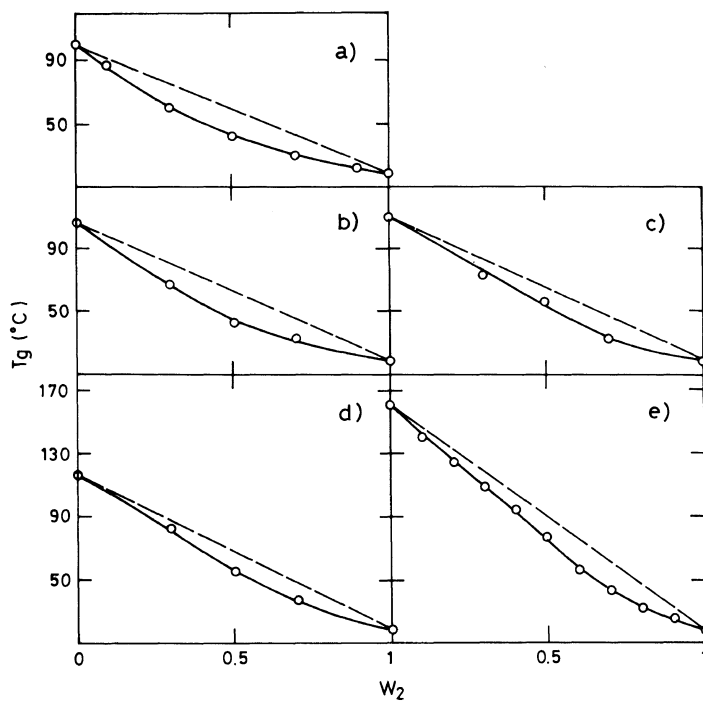


Figure 6. T_g as a function of the weight fraction of PMA in the blend, w_2 . a) HSMS67+PMA, b) HSMS60+PMA, c) HSMS52+PMA, d) HSMS37+PMA, and e) P4HS+PMA.¹⁸

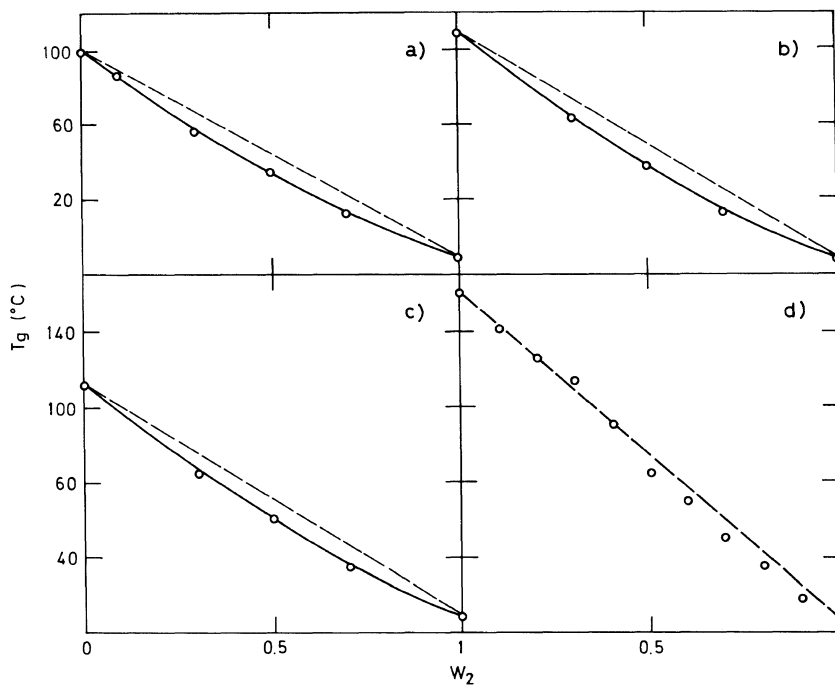


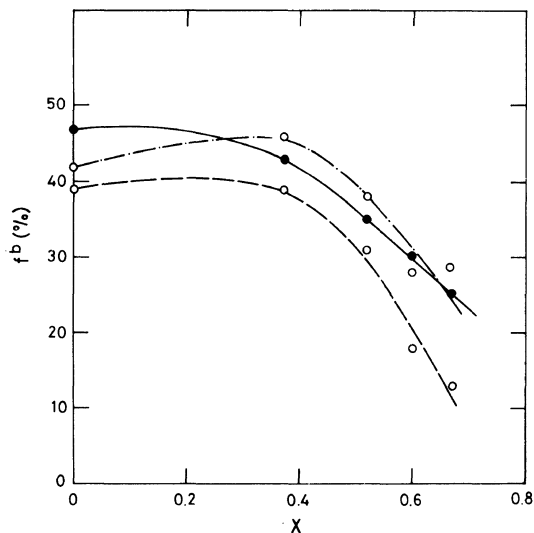
Figure 7. T_g as a function of the weight fraction of PEA in the blend, w_2 . a) HSMS67+PEA, b) HSMS60+PEA, c) HSMS52+PEA, and d) P4HS+PEA.¹⁸

Table III. Percentage of hydroxyl groups autoassociated and associated with carbonyl groups and Kwei equation parameter, q , for the systems

Blends ($w_2 = 0.5$)	-OH autoassociated/%	-OH associated with carbonyl groups/%	q
P4HS + PMA	46	54	-48
HSMS37 + PMA	14	86	-48
HSMS52 + PMA	10	90	-48
HSMS60 + PMA	37	63	-64
HSMS67 + PMA	44	56	-68
P4HS + PEA	50	50	-32
HSMS37 + PEA	13	87	—
HSMS52 + PEA	8	92	-40
HSMS60 + PEA	16	84	-44
HSMS67 + PEA	~0	~100	-40
P4HS + PVA	35	65	-64
HSMS37 + PVA	5	95	—
HSMS52 + PVA	~0	~100	-56
HSMS60 + PVA	~0	~100	-56
HSMS67 + PVA	~0	~100	-48

III shows the fraction of hydroxyl groups that do not bond to carbonyl ones. This fraction was calculated from the degree of modification, percent of associated C=O (Table II) and blend composition, and may be considered as the fraction of autoassociated hydroxyl groups since no free -OH groups are detected (see Figure 3). It can be observed that for blends of P4HS with PEA or PMA, around 50% of the -OH groups are involved in -OH---OH bonds, while for PVA, this fraction is smaller. This fraction decreases when the degree of substitution of -OH groups by -OCH₃ ones in P4HS increases. The importance of the effect of methoxylation decreases from PVA blends to PEA blends and even more in PMA blends. This means, that PMA is less effective than PEA and PVA to destroy the autoassociation in blends that involve modified P4HS.

In summary, the present FT-IR results clearly show that the modification of P4HS reduces -OH---OH and -OH---C=O bond formation. It is also observed that in all blends,

**Figure 8.** Fraction of H-bonded carbonyl groups, f^b as a function of the degree of methoxylation of P4HS, X , for blends with: PVA (—), PMA (---), and PEA (- · -).

most of hydroxyl groups bond to carbonyl ones, which explains the miscibility of the systems. Finally, in Figure 8 it can be observed that fraction of bonded carbonyl groups in blends with 37% modified P4HS is the same or even higher than for non-modified P4HS, even though the total number of -OH groups is smaller. This is a consequence of the decrease in the tendency to autoassociation in the blends with modified P4HS. These results are consistent with those reported for blends of poly(styrene-*co*-4-hydroxystyrene) and poly(*n*-alkylmethacrylate)s blends. In these cases the immiscibility appears only when the fraction of 4-hydroxystyrene in the copolymer is smaller than 2%.²⁶

The difference between the values of the frequency corresponding to the maxima of the bands of free and associated carbonyl groups, $\Delta\nu = \nu^{\text{free}} - \nu^{\text{assoc}}$, is a measure of the strength of hydrogen bonds.⁶ $\Delta\nu$ in Tale II show that, within experimental accuracy, the strength of the hydrogen bonds is not affected by the degree of modification of P4HS, although it seems to be larger for blends with PVA than for those with PEA or PMA. In similar

systems²⁷ the differences in the value of Δv have been related with the accessibility of the carbonyl group.

To discuss the results obtained by DSC and FT-IR, we must consider the relation between T_g behavior and interactions in the blends.

The glass transition behaviour of several polymer blends has been reviewed by Schneider *et al.*²⁸ They assume that segmental alignment by directional specific interactions between the two different polymer chains contributes to reduction of the free volume and consequently to decrease of the mobility in the polymer blend. Thus, a positive deviation in the T_g -composition curve may be expected when strong hydrogen bonding or charge transfer interactions take place between polymers in the blend. But in the case of highly autoassociated polymers, the destruction of autoassociation by other components gives a positive contribution to the free volume that should be taken into account. Consequently, T_g behavior of compatible blends is the result of a balance between the two factors considered above. Two examples illustrate these effects. (a) For P4HS-poly(4-vinyl pyridine) blends⁷ the interaction between the two polymers is so strong that can lead to stable complexes, manifesting as an upwards curvature in the T_g -composition behavior. (b) When P4HS is blended with poly(butylene adipate)²⁹ weaker hydrogen bonds between two polymers lead to the opposite behavior.

Several equations have been proposed to predict the T_g -composition dependence of miscible polymer blends.^{28,30-33} The systems with specific interactions are usually well represented by the Kwei equation³³:

$$T_g = ((w_1 T_{g1} + K w_2 T_{g2}) / (w_1 + K w_2)) + q w_1 w_2 \quad (2)$$

The first term on right-hand side of eq 2 is identical with the widely used Gordon-Taylor equation and the second one accounts for specific interactions in the mixture. For systems with no inflection point on the T_g vs. w_1 curve

(eq 2) is simplified taken $K=1$ ³³:

$$T_g = (w_1 T_{g1} + w_2 T_{g2}) + q w_1 w_2 \quad (3)$$

The term in brackets represents additivity and q is a parameter that is positive when, in average, the interactions between chains of the different polymers are stronger than those between chains of the same polymer; otherwise $q < 0$. In all systems studied in this work we obtained $q < 0$ that can be understood considering that miscibility is due to the equilibrium reached between the number of strong -OH---OH bonds broken and the number of weaker -OH---C=O bonds formed (see Table III). Since the additivity law may correspond to a case in which contact energies between polymers after blending are similar to contact energies in homopolymers, $q < 0$ and therefore $T_g < (w_1 T_{g1} + w_2 T_{g2})$ may be expected.

Coleman *et al.*²³ suggest that the miscibility of blends of P4HS and poly(*n*-alkylacrylate) decreased with increasing the pendant group size in the polyacrylate because of increasing steric difficulty in the formation of -OH---C=O bonds. This is according to T_g vs. w_2 behavior shown in Figures 6 and 7 for the P4HS + PMA and P4HS + PEA systems. Table III indicate that the fraction of hydroxyl groups involved in -OH---C=O bonds decrease from PMA to PEA. The opposite behaviour is shown for the difference between T_g and the additive value of T_g , and therefore of the q parameter. This is more evident for the P4HS + PVA system where a lower fraction of hydroxyl groups is involved in -OH---OH bonds. This system shows the more negative q value and consequently the larger difference between the experimental T_g and the additive value.

The differences in T_g vs. w_2 curves for the systems in which P4HS is involved, is less evident in systems with P4HS modified due to the lower degree of autoassociation present in these systems (see Table III).

CONCLUSIONS

FT-IR and T_g data confirm that blends formed by P4HS or methoxylated P4HS with PVA or PMA or PEA are miscible throughout the whole composition range. The formation of hydrogen bonds between hydroxyl groups of P4HS and carbonyl groups of the other polymers is the driving force of miscibility.

There is a qualitative correlation between the fraction of $-\text{OH}---\text{OH}$ bonds remaining after blending and departure of the T_g vs. w_2 curves from additivity T_g equation. In blends of P4HS with PVA, PMA, and PEA, fraction $-\text{OH}---\text{OH}$ bonds increase in the order PVA to PMA to PEA. The opposite behaviour is shown for the difference between experimental T_g and that calculated through $T_g = w_1 T_{g1} + w_2 T_{g2}$.

The methoxylation of P4HS leads to significative reduction in $-\text{OH}---\text{OH}$ bonds in the homopolymer. This compensates for the reduction in $-\text{OH}---\text{C}=\text{O}$ bonds, with consequently similar T_g vs. w_2 behaviour.

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