

NOTE

*Thermostability of Poly(*p*-Hydroxystyrene) Blends with Poly(vinyl Pyrrolidone) and Poly(ethyl Oxazoline)*

It is generally accepted that interchain hydrogen bonding restricts segment mobility and alters the glass transition temperatures and viscoelastic responses of polymers.¹⁻⁴ On the other hand, the attendant changes in the thermal stabilities of some polymers are not completely understood. Barb⁵ found that hydrophilic groups introduced into the aromatic ring increased the thermal stability of polymers. Still and Whitehead^{6,7} found the pyrolysis behavior of poly(hydroxystyrene), PHS, in the temperature range of 300–500°C to be different from that of polystyrene.

Whether interpolymer hydrogen bonding in a blend will result in the alteration of thermal stability is an open question. As early as 1959, it was reported that blends of poly(acrylic acid) and poly(ethylene oxide) containing 30–70% of the latter exhibited better thermal stability than either component polymer.⁸ PHS is miscible with poly(vinyl pyrrolidone) (PVP) and poly(ethyl oxazoline) (PEOx), and the driving force for miscibility can be attributed to hydrogen-bonding interaction between the donor polymer PHS and the acceptor polymers. In this communication we wish to report preliminary results of an investigation of the thermal stability of these blends. Thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) were used to determine weight loss and chemical changes.

EXPERIMENTAL

PHS was prepared by hydrolysis⁹ of poly(*p*-acetoxystyrene) (MW 5×10^5) which was polymerized from *p*-acetoxystyrene (courtesy of Celanese Co.) by free radical initiator. The polymer was purified by precipitation twice from methyl ethyl ketone solution into a large excess of hexane. PVP (MW 3.6×10^5) and PEOx (MW 5×10^5) were obtained from Aldrich Co. and Dow Chemical Co., respectively.

A du Pont 1090 Thermal Analyzer equipped with TGA model 951 was employed for thermostability studies. A heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min were used. FTIR spectra were recorded on a Digilab FTS-60 FTIR spectrometer. Sixty scans at a resolution of 2 cm⁻¹ were signal-averaged and stored on a magnetic disk system. The frequency scale is internally calibrated with a reference helium-neon laser to an accuracy of 0.2 cm⁻¹. A high temperature cell mounted in the spectrometer was employed to obtain spectra at elevated temperatures and each temperature was maintained for 3 min.

Tetrahydrofuran (THF) was used to cast thin films on potassium bromide of PHS, PHS-PVP, and PHS-PEOx blends. After the solvent had evaporated at room temperature the films were put in a vacuum oven at 50°C for one week to remove residual solvent. The samples were stored in a vacuum desiccator.

RESULTS AND DISCUSSION

Still and Whitehead mentioned⁶ that all samples of PHS should be dried in two stages to remove solvent before TGA measurement. The recommended drying procedure consisted of two steps, 70°C/0.1–0.3 mmHg to constant weight, then 160°C/0.1 mm Hg to constant weight. In following their procedure, we noticed that the dried samples were no longer completely soluble in THF. Therefore, two samples were prepared: Sample 1 dried in one stage (at 60°C in vacuum to constant weight) and Sample 2 in two stages (at 60°C, and then 160°C in vacuum to constant weight). The TGA curve of Sample 1 (Fig. 1) shows an initial weight loss of 6% between 160 and 240°C followed by more rapid degradation beginning at 360°C. This is in contrast with the TGA curve for Sample 2, which shows no change in weight until 360°C. At temperatures above 400°C, rapid degradation occurs in both samples and the TGA curves coincide with each other. In view of the chemical reaction taking place during the preparation of Sample 2, which leads to

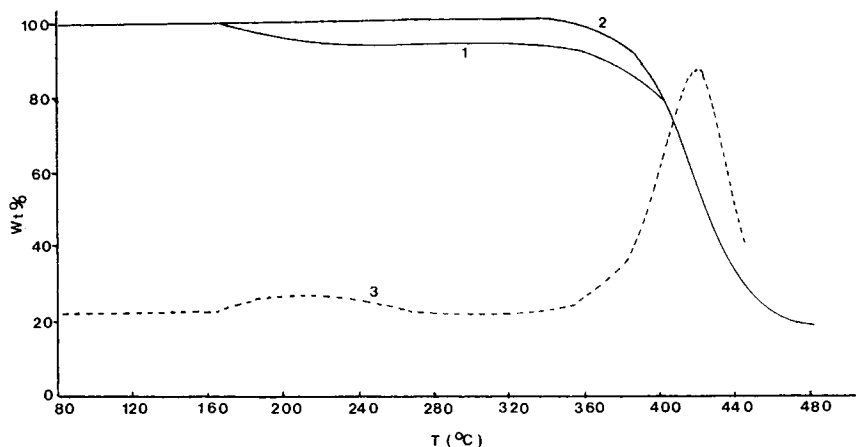


Fig. 1. The weight loss curves for PHS after different drying conditions (heating rate $10^{\circ}\text{C}/\text{min}$, in nitrogen). (1) dried at 60°C in vacuum to constant weight; (2) dried at 60°C in vacuum to constant weight, then at 160°C in vacuum to constant weight; (3) derivative curve of Sample 1.

crosslinking, the weight loss of Sample 1 around 200°C cannot be simply ascribed to retained solvent or water.

The FTIR spectra of PHS at room temperature duplicated that reported by Moskala et al.¹⁰ The bands in the $1100\text{--}1300\text{ cm}^{-1}$ region are typical of phenols in the solid state. For clarity of presentation, this region was expanded (Fig. 2). The broad band was attributed to OH deformation and C—O stretching vibration which overlapped to some degree, while the sharp peak (1172 cm^{-1}) was assigned to the aromatic ring.^{10,11} As temperatures increased, the broad peak decreased gradually and a new peak (1251 cm^{-1}), characteristic of C—O—C asymmetric stretch¹¹ appeared at 200°C . It indicated that ether groups were formed above 200°C via crosslinking reactions involving the hydroxyl groups of PHS. The loss of hydroxyl groups is reflected in the diminished area of the absorption peak in the $3100\text{ to }3600\text{ cm}^{-1}$ region. This peak encompasses both the "free" and self-associated hydroxyl absorptions. The area of the peak decreased by about 44% upon heating PHS from room temperature to 250°C in nitrogen. We are unable to analyze the IR results quantitatively because of the complexity of the overlapped absorption and a lack of knowledge of the extinction coefficients of the "free" and self-associated species. But the magnitude of the area change is coincidentally in agreement with the weight loss data determined by TGA.

Films of PVP, PEOx, and their blends with PHS were cast from 5% THF solution, dried at 60°C in vacuum to constant weight. The TGA curves of those blends are shown in Figure 3 and the TTK data are summarized in Table I. The curves for PVP and PEOx are not shown in Figure 3 because the weight loss was not measureable below 360°C for each polymer. From Figure 3 and Table I, we could see that the weight loss of PHS in the temperature range $200\text{--}250^{\circ}\text{C}$ decreased for the blend. For PHS : PVP = 1 : 2 (by weight) and PHS : PEOx = 1 : 4 (by weight), the blends suffered no weight loss at 200°C . On the other hand, the onset temperatures of rapid decomposition of the blends, generally from $380\text{ to }420^{\circ}\text{C}$, were not influenced significantly by compositions. Apparently intermolecular hydrogen bonding between the OH in PHS and the $>\text{C}=\text{O}$, and

$$>\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-$$
 in PVP and PEOx still exerted an effect on ether formation, and consequently improved the thermal stability of PHS in the range $200\text{--}250^{\circ}\text{C}$. At higher temperature, for example, 380°C , such an effect was no longer operative, because of hydrogen bond dissociation.

The FTIR spectra of PHS-PVP recorded at the same conditions as that of PHS, seemed to support the above explanation. Hydrogen bonding in PHS-PVP did not disappear completely even at $200\text{--}250^{\circ}\text{C}$ (Fig. 4). The ether absorption bands in the region of $1100\text{--}1300\text{ cm}^{-1}$ for PHS-PVP blends were determined by using a subtraction procedure¹² to obtain a difference plot of blend minus PVP [Fig. 5(a)–(c)]. In comparing Figure 5(c) with Figure 2, we found that the intensity of the ether band (1251 cm^{-1}) in PHS-PVP above 200°C was lower than that in PHS.

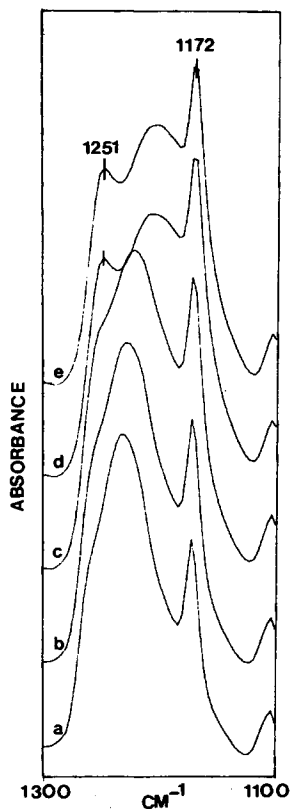


Fig. 2. FTIR spectra of PHS recorded in the $1300\text{--}1100\text{ cm}^{-1}$ region at (a) room temperature, (b) 100°C , (c) 160°C , (d) 200°C , and (e) 250°C in nitrogen.

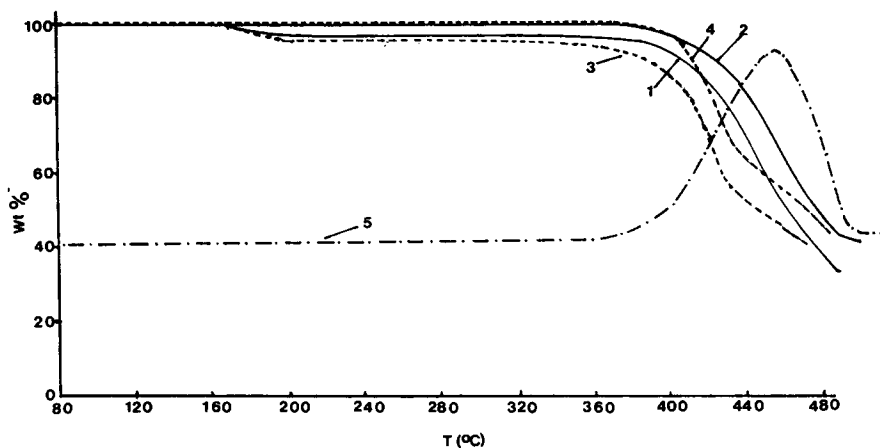


Fig. 3. TGA curves of blends (normalized to PHS weight loss; heating rate $10^\circ\text{C}/\text{min}$. in nitrogen). (1) PHS-PVP blend (1:1w/w); (2) PHS-PVP blend (1:2w/w); (3) PHS-PEOx blend (1:0.8w/w); (4) PHS-PEOx (1:4w/w); (5) derivative curve of Sample 2.

TABLE I
TGA Data of Poly(*p*-Hydroxystyrene) (PHS), Poly(vinyl Pyrrolidone) (PVP),
Poly(ethyl Oxazoline) (PEOx) and Blends^a

Sample	Weight loss (%), below 360°C		T_d (onset) °C
	As measured	Normalized to PHS	
PHS	6.0		391
PVP	0		420
PEOx	0		408
PHS-PVP (1:0.5w/w)	3.0	4.5	399
PHS-PVP (1:1w/w)	1.5	3.0	405
PHS-PVP (1:2w/w)	0	0	413
PHS-PEOx (1:0.8w/w)	3.0	5.4	383
PHS-PEOx (1:1.5w/w)	1.0	2.5	380
PHS-PEOx (1:4w/w)	0	0	387

^aHeating rate, 10°C/min, in nitrogen.

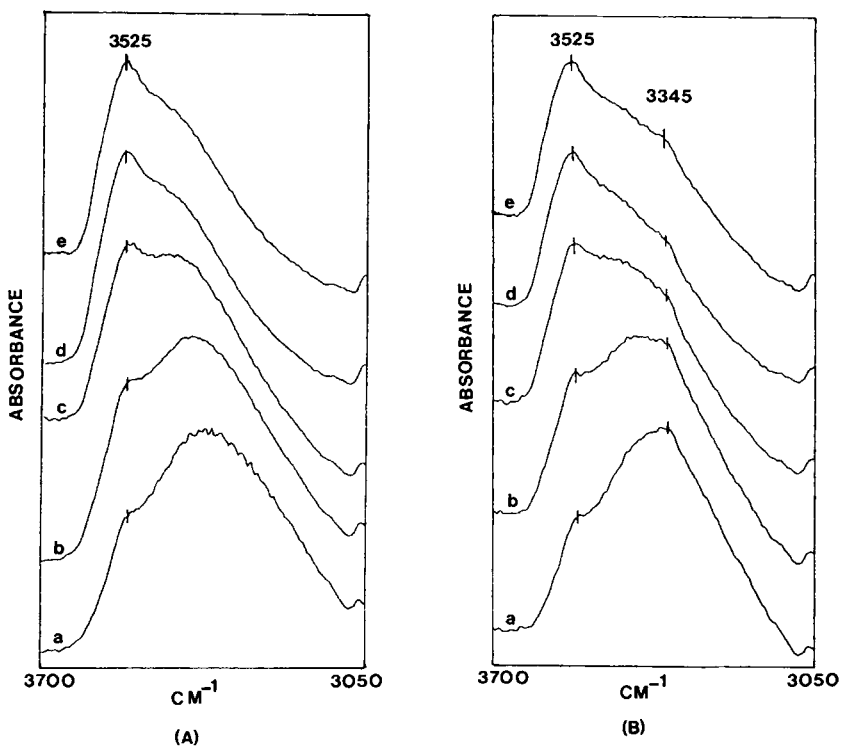


Fig. 4. FTIR spectra of (A) PHS and (B) PHS-PVP (1:1w/w) blend in the 3700–3050 cm^{-1} region recorded at (a) room temperature, (b) 100°C, (c) 160°C, (d) 200°C, and (e) 250°C in nitrogen.

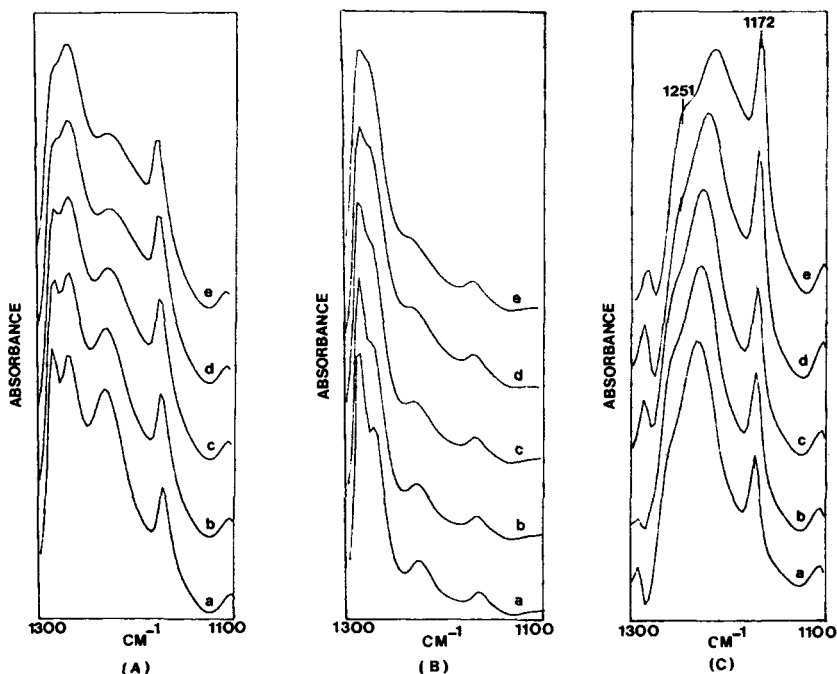


Fig. 5. FTIR spectra of (A) PHS-PVP (1 : 1w/w) blend, (B) PVP, and (C) subtraction plot of (A) minus (B) in the 1300–1100 cm^{-1} region recorded at (a) room temperature, (b) 100°C, (c) 160°C, (d) 200°C, and (e) 250°C in nitrogen.

We also obtained similar results for the PHS-PEOx blend. This can be construed as evidence for reduced crosslinking reaction in the blend by the hydrogen-bonding effect.

CONCLUSIONS

It was found that a loss in the weight of the PHS of about 6% in nitrogen in the temperature range 200–250°C was caused by the crosslinking reaction involving hydroxyl groups to form ethers. This phenomenon vanished when PHS was mixed with PVP (1 : 2 w/w) or PEOx (1 : 4 w/w). Evidence for an intermolecular hydrogen-bonding effect on the thermostability of PHS was obtained by FTIR studies.

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K. J. ZHU
T. K. KWEI
E. M. PEARCE

Polymer Research Institute
and Department of Chemistry
Polytechnic University
333 Jay Street
Brooklyn, New York 11201

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