

NOTES

Thermal Degradation of Poly(*N*-vinylpyrrolidone)–Poly(vinyl alcohol) BlendsVijayalaxmi RAO,[†] P. LATHA, P. V. ASHOKAN, and M. H. SHRIDHAR*Department of Materials Science, Mangalore University, Mangalagangothri,
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Thermal stability and decomposition behavior of blends of poly(vinyl alcohol) (PVA) and poly(*N*-vinylpyrrolidone) (PVP) have been studied. Decomposition behavior of the blends was different from that of individual polymers. Addition of PVP to PVA effectively increases the initial thermal decomposition temperature and temperature corresponding to 50% decomposition. There is thus strong interaction between components. Effect of blend composition on the amount of residue remaining at various temperatures was studied. There is a linear increase in the amount of residue with increasing proportion of PVP. Activation energy was calculated for the first degradation step using Horowitz–Metzger and Coats–Redfern Equation. Activation energies of the blends in the entire composition range are higher than the corresponding values of individual polymers.

Thermal properties of polymers give valuable information regarding stiffness, toughness, stability and compatibility in blends.^{1–4} A detailed understanding of thermal degradation of polymers is important as the polymer is subjected to thermal history during manufacture and processing. Blending has great influence on the thermal stability of polymers and thermal stability of blends depends strongly on interaction between the individual polymers.^{5,6}

EXPERIMENTAL

Blend films of PVP and PVA were prepared by solution casting using common solvent, distilled water. Blends of PVP/PVA in all compositions, namely 100/0, 80/20 (B2), 60/40 (B4), 50/50 (B5), 40/60 (B6), 20/80 (B8), and 0/100 were prepared by mixing the required amounts of 5% solution of PVP and PVA in correct proportions. The blend films were dried and preserved in vacuum desiccator. Clear transparent films were obtained. Thermogravimetric analysis (TGA) and Derivative Thermogravimetric analysis (DTG) of the films were carried out in Shimadzu DT-40 thermal analyzer in N₂ atmosphere at a heating rate of 10°C min⁻¹. The amount of the samples taken for experiments were 5 mg. The thermograms were taken for constituent polymers and for blends of various compositions.

RESULTS AND DISCUSSION

The data obtained from thermogravimetric analysis

are given in Figure 1. The initial thermal degradation peak temperature of PVA is about 200°C and associated mainly with dehydration accompanied by formation of volatile products.⁷ In the present study, the initial degradation peak is observed at about 200°C. On blending with PVP, the degradation peak shifted to the higher temperature side. In the case of PVA, weight loss due to thermal degradation was about 73% at 400°C. But in the case of PVP, the weight loss is only about 30% at 400°C. Weight loss at 350°C for 100% PVA and Blends B8, B6, B5, B4, B2, and PVP was 51, 42, 38, 36, 30, 25, and 14.5% respectively. *T*₀ (Initial thermal decomposition peak temperature), and *T*₅₀ (temperature corresponding to 50% weight loss) were plotted against PVP weight percentage (Figures 2 and 3).

Increase in PVP content effectively increases *T*₀ and *T*₅₀ in the blend (Table I). Figure 4 and Table II show the effect of blend composition on the amount of residue remaining at various temperatures. The graph shows a linear increase in the amount of residue at 300°C, 350°C, and 400°C with PVP. Blending changes the decomposition behavior of PVA; it improves the thermal stability. This enhancement in thermal stability of PVA on adding PVP is associated with strong interaction between PVA and PVP. Activation energy is calculated for the first degradation step using Horowitz–Metzger and Coats–Redfern Equations^{8,9} (Table III). Horowitz and Metzger derived the following equation:

$$\ln[1 - (1 - \alpha)^{1-n}] = \frac{-E\theta}{RT_s^2} + \ln(1-n) \quad (\text{for } n \neq 1)$$

and

$$\ln[-\ln(1-\alpha)] = \frac{-E\theta}{RT_s^2} + C \quad (\text{for } n = 1)$$

Coats–Redfern Equation is given by

$$\log\left(\frac{-\log(1-\alpha)}{T^2}\right) = \log\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{2.303RT} \quad (\text{for } n = 1)$$

*E*_a represents the apparent activation energy of decomposition. In the present investigation, plots of ln[−ln(1−α)] versus θ and log[−log(1−α)/T²] versus 1/T were linear showing that n=1. Activation energy was higher for blends than individual polymers (Figure 5), again indicating strong interaction between the blends. Variation of *E*_a may be due to the degree of compatibility in the blends. Maximum compatibility may

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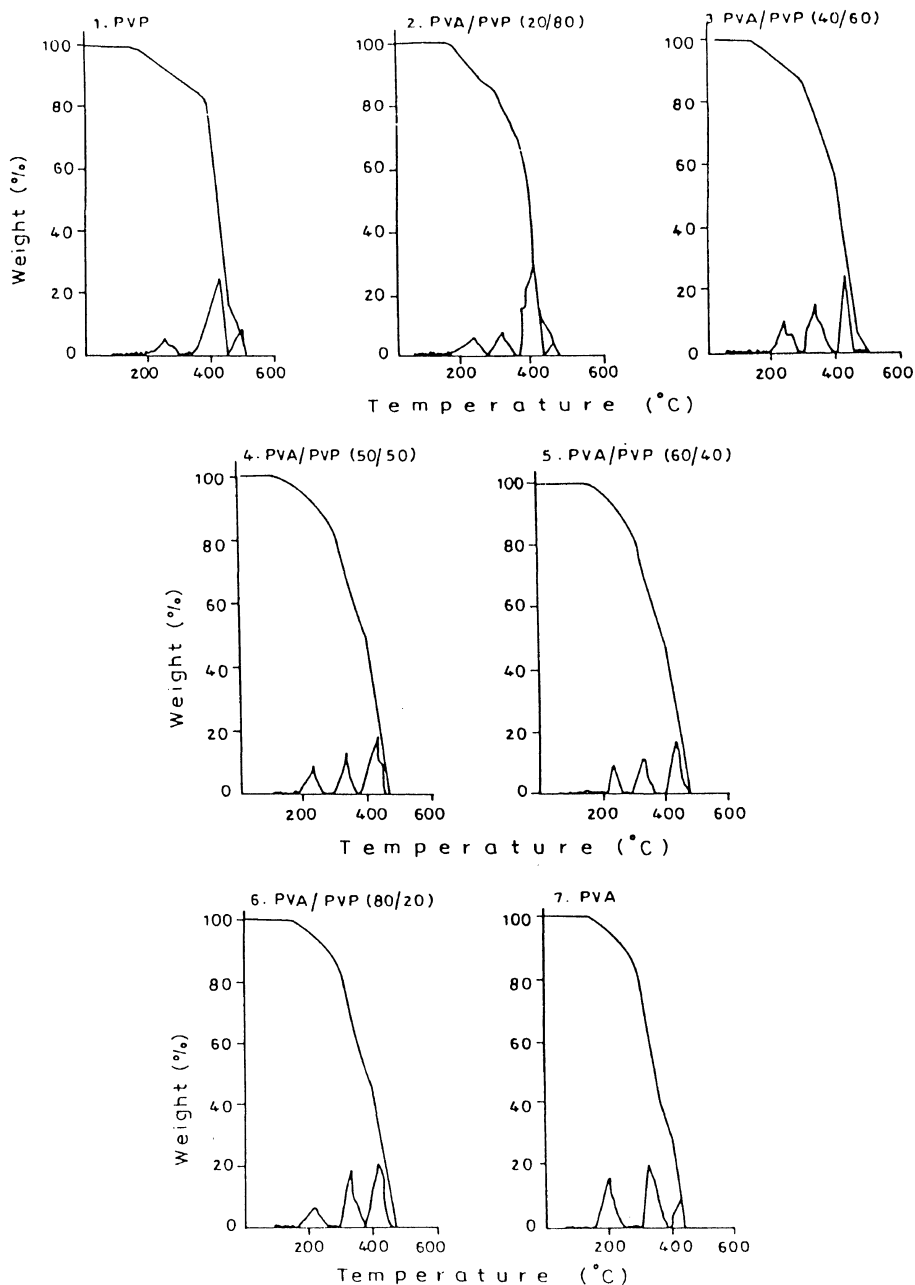


Figure 1. Thermal degradation steps for PVP, PVA, and blend.

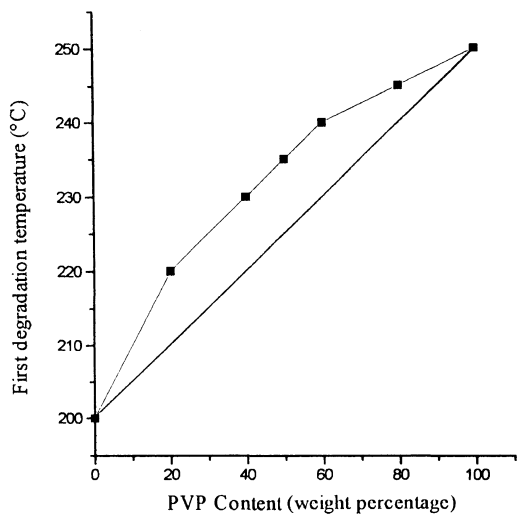


Figure 2. T_0 vs. PVP weight percentage.

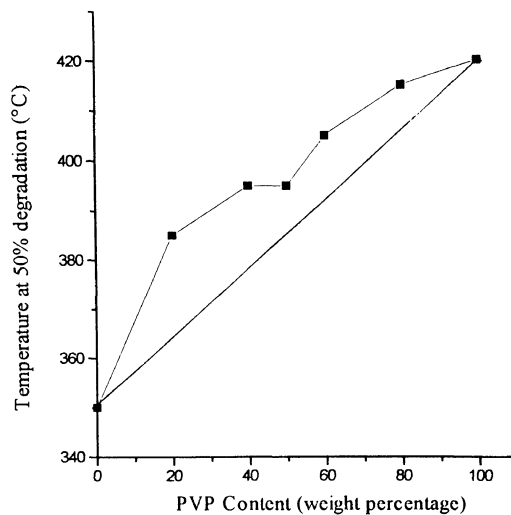


Figure 3. T_{50} vs. PVP weight percentage.

Table I. T_0 and T_{50} for PVP and blends

Polymer blend	First degradation temperature in °C	Temperature in °C when degradation is 50%
	T_0	T_{50}
PVP	250	420
B2	245	415
B4	240	405
B5	235	395
B6	230	395
B8	220	385
PVA	200	350

Table II. Residue weight percentage for PVP, PVA, and blends at different temperatures

Polymer blend	Residue weight percentage at		
	300°C	350°C	400°C
PVP	89	85.5	69.5
B2	86	75	60
B4	85	70	55
B5	82.5	64	45
B6	84	62	47.5
B8	83.5	58	44
PVA	80	49	27.5

Table III. Calculated activation energy for PVA and their blends

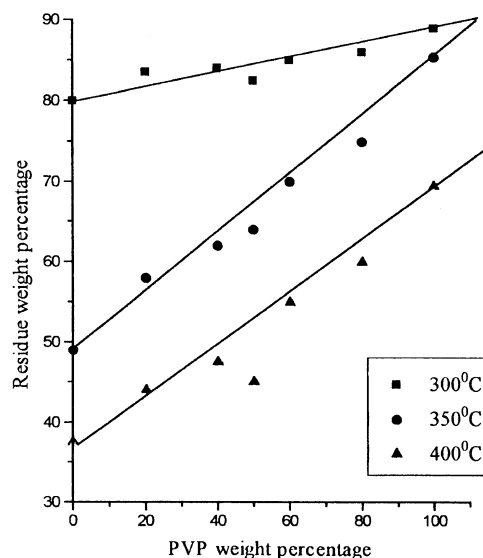
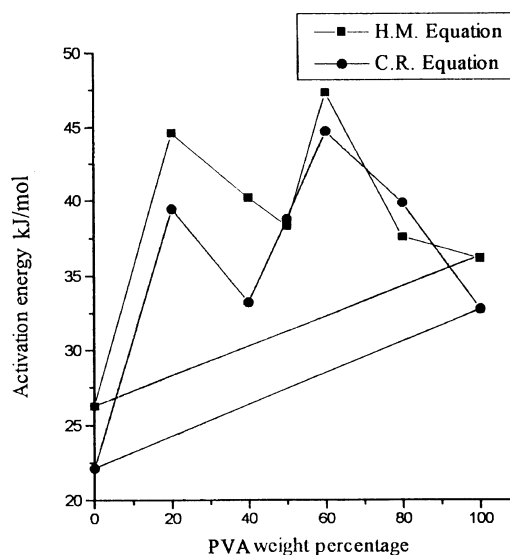
Polymer blends	Activation energy	
	Horowitz-Metzger Equation	Coats-Redfern Equation
PVP	26.24	22.17
B2	44.62	39.49
B4	40.22	33.26
B5	38.31	38.8
B6	47.33	44.76
B8	37.59	39.9
VPA	36.17	32.81

be for B2 and B6 (20%PVA : 80% PVP and 40% PVA : 60% PVP). Similar results have been reported for Blends of PVC and poly(methyl methacrylate) (PMMA).¹⁰

In conclusion, the thermal stability and decomposition behavior of PVA were improved by the addition of PVP. Activation energies of blends in the entire composition range are higher than the corresponding values of individual polymers. Thus there is strong interaction between PVA and PVP and PVA forms miscible blends with PVP throughout the entire composition range.

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Figure 4. Residue weight vs. PVP weight percentage.

Figure 5. Activation energy vs. PVA weight percentage.

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