Thermal Degradation of Water Soluble Polymers and Their Binary Blends

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ABSTRACT: The effect of five different metal oxides on the pyrolysis of poly(ethylene oxide) (PEO), polyacrylamide (PAM), and poly(vinyl alcohol) (PVA) was investigated using thermogravimetry. The presence of metal oxide did not influence the degradation of PEO while the order of metal oxide on the degradation rate of PAM and PVA was PbO $> Co_3O_4 > CuO > ZnO > Al_2O_3$. The miscibility and the decomposition of PEO–PAM and PVA–PAM blends were also investigated. The blends were found to be immiscible and the presence of one polymer did not influence the degradation of the other polymer in the polymer blend. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 233–240, 2006

Key words: degradation; water soluble polymers; oxides

INTRODUCTION

Thermal degradation of polymers is widely studied because of both academic and industrial interest. The thermal degradation of polymers is influenced by a variety of factors including mode of synthesis, molecular weight, presence of additives or impurities, presence or absence of oxygen, etc. Some factors stabilize while other factors accelerate degradation depending on the type of polymer and the mechanism of thermal degradation. Interaction between individual polymers in blends can significantly alter the properties and consequently influence the applications. Poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), and polyacrylamide (PAM) are water-soluble polymers of interest especially because of their increasing biomedical applications. There are only a few studies on the thermal degradation of their blends or the polymers with additives.

The thermal degradation of PEO occurs at a lower temperature when compared to other polymers without an ether backbone. The C—O bonds are weaker and more susceptible for breakage.[1] Comparison between degradation products of low and high weight PEO shows that the mechanism of degradation is similar.[1,2] A ^{13}C NMR study of thermo oxidative degradation of PEO showed formation of hydroxy and formate ester end groups, with the latter predominating among the products.[3,4] IR-spectra shows evidence for formation of aldehyde, carboxylic, and hydroxyl groups.[5] Complexation with metal salt reduces the thermal stability of PEO, with the anion exerting a greater influence than the cation.[6] In all the earlier mentioned cases, degradation occurs by random chain scission along the polymer backbone with the breakage of either C—C or C—O bonds.

The thermal degradation of PAM proceeds in three stages, the first stage essentially being the removal of adsorbed water. The second stage (at temperatures between 200 and 300°C) involves release of ammonia, water, and cyclization to form imides. The third stage (above 300°C) corresponds to breakage of polymer backbone resulting in nitriles and release of volatiles like CO_2 and H_2O.[7–9] The activation energy for the degradation of PAM was found to be about 163 kJ/mol.[10,11] Polymers with amide groups are known to be strong absorbers of metal ions, evidenced by color of polymer when colored metal ions were used. The metal ions are probably coordinated with the amide groups.[12,13] The thermogravimetry study of PAM with adsorbed metal ions (from metal nitrates) showed that the ions exert a stabilizing effect on the polymer. The strength of the metal ion-polymer complex was inversely proportional to radius of the main group metal ions. The transition metal ions, however, showed dependence on ligand field stabilization energy rather than on the ionic radius.[14] A study with three different transition metal chlorides, where the ionic radius of the metal ion varied only between 0.69 and 0.74 Å, showed an increasing stabilizing effect with decrease in ionic radius.[15]

PVA degrades in two stages, the first stage (270–300°C) corresponding to elimination of hydroxyl side groups and the second stage (above 380°C) resulting in the degradation of the polyene backbone. The major

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degradation products are identified as saturated and unsaturated aldehydes and ketones, along with the formation of water. Conjugation in the backbone chain after the first stage was also detected.[16–18] The initial molecular weight and the hydrolysis degree influenced the thermo-oxidative degradation of PVA under dynamic thermogravimetric conditions. Higher molecular weight caused greater complexity in the degradation process whereas higher hydrolysis degree reduced the decomposition temperature of PVA.[19,20] The activation energies for the first and second stage were about 154 and 133 kJ/mol, depending on the degree of conversion in the respective stages.[21]

Polymer compatibility is an important criterion when dealing with blends. The miscibility is usually determined by the existence of a single glass transition temperature, which is between the glass transition temperatures of the individual polymers. Miscibility can also be discerned when a decrease in melting point is observed due to the presence of crystallines like PEO. The miscibility of PEO and PVA is not clear with studies based on melting and crystallization indicating partial miscibility[22] and studies based on thermal and spectroscopic methods indicating immiscibility of the polymer mixture.[23,24] It was suggested[25] that only polymers with primary hydroxyl groups could form hydrogen bonds with the ether oxygen of PEO. The miscibility of PAM with PVA is also inconclusive[26] with an indication that the miscibility would depend on the rate of water evaporation during film preparation. However, when a lower molecular weight (~2000) of PEO/Polyethylene glycol was used, the blend showed partial miscibility. This indicates that the study of miscibility of these polymers would be interesting.

The polymers chosen have varied applications and are used in diverse fields such as textile, pharmaceutical, paints, oil and gas and electronics and telecommunication industry, etc. Impurities such as metal oxides are commonly found. Further, these polymers are sometimes used together. Thus, it becomes imperative to study the influence of one polymer on the degradation of the other polymer and the influence of metal oxides on the degradation of the polymer. Thus the objective of the current study is to investigate the effect of metal oxides on the pyrolytic degradation of three water soluble polymers (PEO, PAM, and PVA). The miscibility and the thermal degradation of the binary blends of these polymers (PEO–PAM and PVA–PAM) was also examined to determine the interaction between these polymers.

EXPERIMENTAL

Materials

Polyethylene oxide ($M_v \sim 2 \times 10^5$ g/mol) and PVA ($M_n \sim$ 90,000 g/mol, 99% hydrolyzed) were obtained from Sigma Aldrich chemicals (USA). Polyacrylamide was synthesized as described elsewhere.[27] The number-average molecular weight was around 1.5×10^5 g/mol as determined from GPC (described later) with polyethylene oxide standards. The anhydrous metal oxides were obtained from S.D Fine Chemicals (India) and were of 99% purity. No further purification of the metal oxides was done prior to use.

Methods

Preparation of films

The films of metal-oxide coated polymer were prepared by solution casting. Appropriate amounts of metal oxide (10%) were mixed with polymer in water and the solvent was evaporated at 60°C until a film of constant weight was obtained. The homogeneity of the films was confirmed by SEM. The binary blends were also prepared in a similar manner by taking appropriate amounts of each polymer to give the desired composition.

Thermogravimetric analysis

All experiments were conducted using a thermogravimetric analyzer (Perkin–Elmer, Pyris Diamond). The nitrogen flow rate was kept constant at 150 cc/min. All experiments were conducted from 25°C to 600°C, under dynamic heating rate of 5°C/min. The reference material used was α-Alumina. The total weight of the sample taken for each experiment was about 6–8 mg.

Differential thermal analysis

The glass transition temperatures of various blends were recorded in a differential scanning calorimeter (Perkin–Elmer, DSC-2). The experiments were carried out in inert atmosphere (N_2) from –100°C to 100°C, in an aluminum pan. The glass transition temperatures were determined by differentiating the DSC signal.

SEM analysis

The homogeneity of the metal oxide coated films and the binary blends was tested using SEM (JEOL, JSM-840A), which was operated with 20 KV. The samples were coated with gold using vacuum evaporator (JOEL, JEE-4X) to aid the conduction during scanning. The SEM pictures (Fig. 1) show a uniform distribution of metal oxides on the polymers suggesting the validity of the preparation method for the metal oxides coated polymers. The SEM pictures of the binary blends (50/50) of PEO–PAM and PVA–PAM are shown in Figure 2.
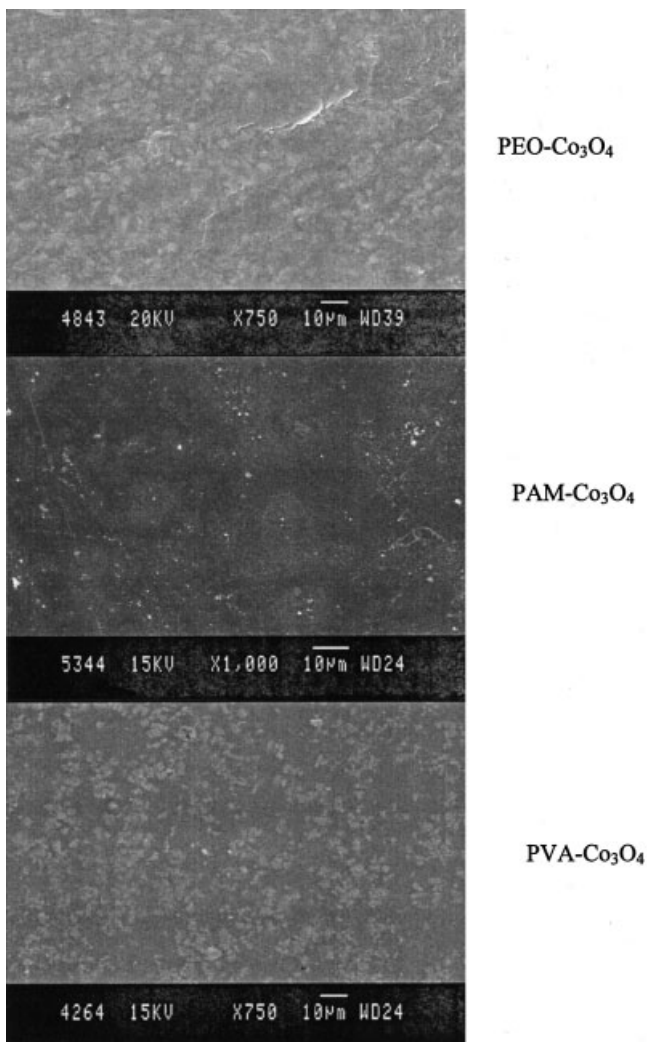
Figure 1 SEM pictures of polymers, PEO, PVA, and PAM coated with the metal oxide, Co_3O_4.

GPC analysis

The samples were analyzed in GPC with double distilled deionized water as eluent at a flow rate of 0.5 mL/min. The columns used were Waters Ultrahydrogel linear SEC columns measuring 7.8 mm $\times$ 300 mm maintained at 50°C. The refractive index was monitored continuously with a Waters 401 Differential Refractometer. About 800 μL of sample was injected into the system to obtain a chromatogram and converted to molecular weight by using polyethylene oxide (Waters) calibration standards.

RESULTS AND DISCUSSION

Thermal studies on metal-oxide coated polymers

The pyrolysis of pure and metal oxide (10%) coated PEO, PVA, and PAM was studied by dynamic thermogravimetric analysis at a heating rate of 5°C/min in an inert nitrogen atmosphere. Figure 3(a)–(c) show the TG profiles for the polymers. While PEO and PVA degrade without leaving any residual mass, PAM degrades leaving a residual mass of around 15 wt %. The degradation of PEO occurs in a single stage while the degradation of PVA and PAM occurs in two stages with the loss of surface bound water occurring below 130°C. The weight loss profile for the degradation of the polymers in the presence of metal oxides is dependent on the type of oxide but does not influence the overall degradation mechanism. The degradation stages are consistent with those found in literature for these polymers.[2,6,9,16,17] The DTG plots for the polymers with different metal oxides are shown in Figure 4(a)–(c). The point of inflection (where the DTG curves passes through a maximum) is taken to be the decomposition temperature (T_d) of the polymer. The T_d's of the pure polymers are 391, 276, and 370°C for PEO, PVA, and PAM, respectively. While the decomposition temperature occurs in the first stage for PVA, it occurs in the second stage for PAM. The decomposition temperature of PEO is relatively unaffected in presence of metal oxides. However, the decomposition temperature of PVA reduces to 239°C when the polymer is coated with PbO. Similarly, the decomposition temperature of PAM reduces to 352°C when the polymer is coated with PbO or Co_3O_4. The variation of decomposition temperature with different metal oxides is shown in Figure 5. A simple trend indicates that the metal
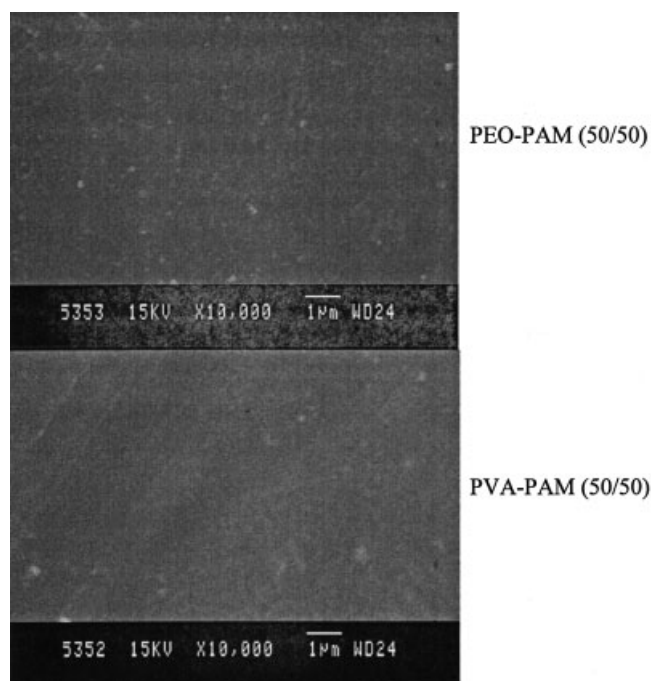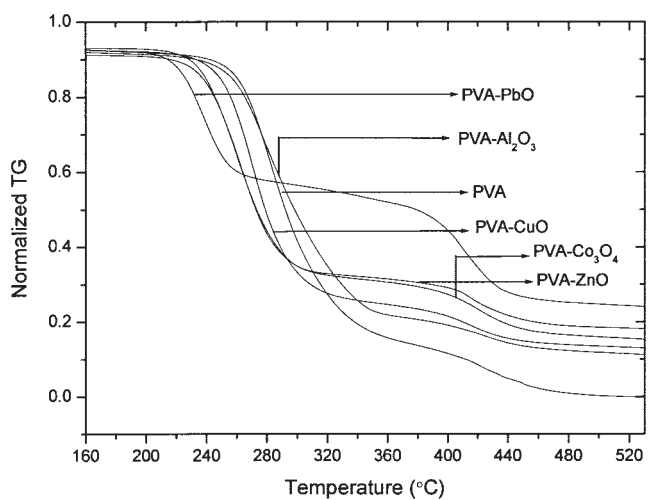

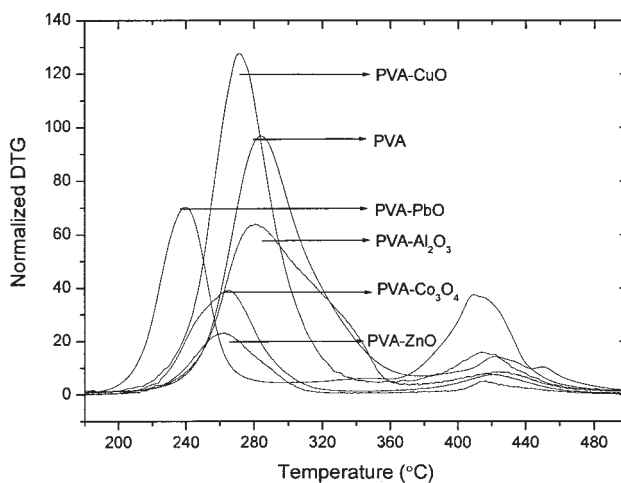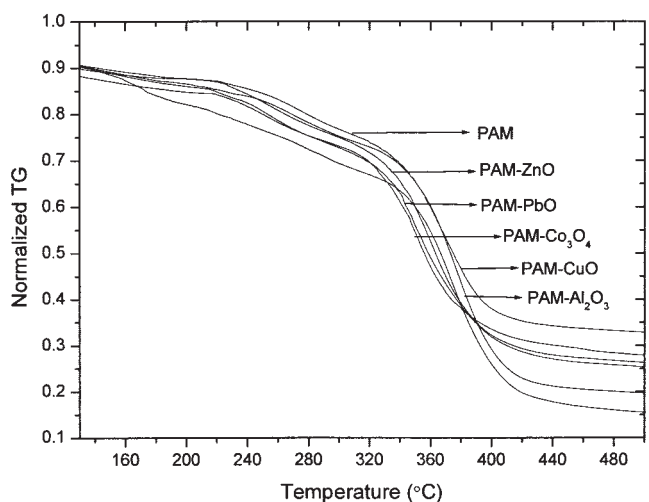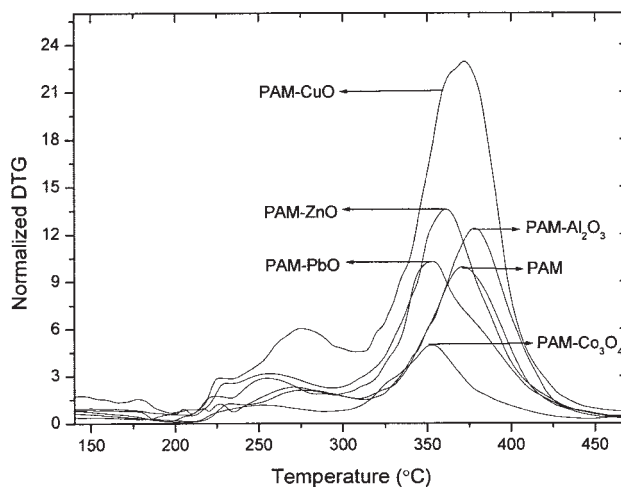**Figure 2** SEM picture of 50/50 blends of PEO–PAM and PVA–PAM.

(a)

(b)
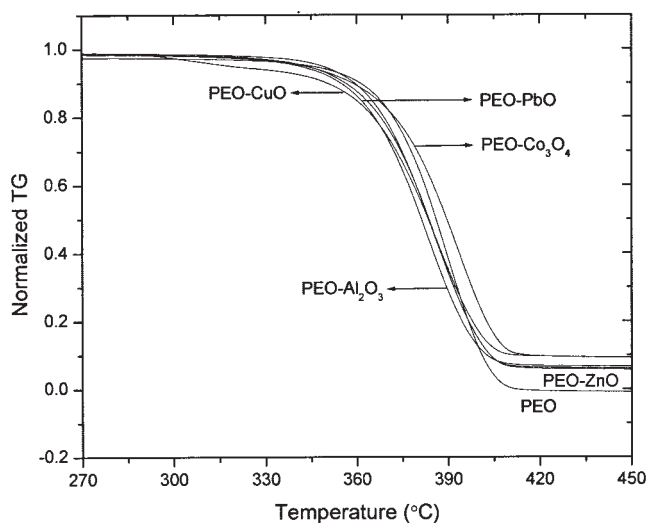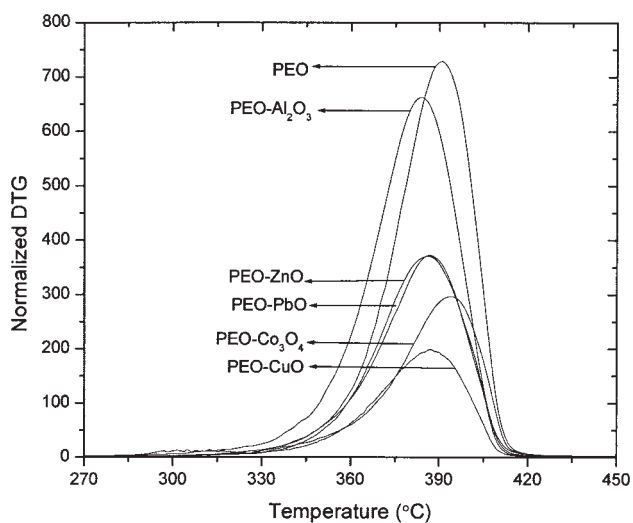
(c)

Figure 3 Thermogravimetric profiles for pure polymers and polymers coated with metal-oxides: (a) PEO, (b) PVA, (c) PAM.

(a)

(b)

(c)

Figure 4 Differential thermogravimetric profiles for pure polymers and polymers coated with metal-oxides: (a) PEO, (b) PVA, (c) PAM.
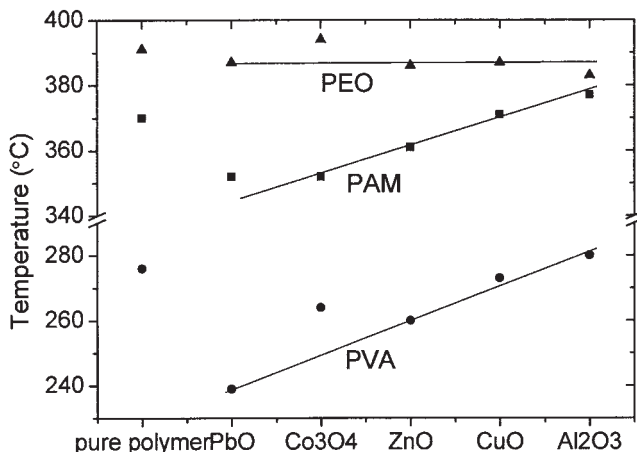
Figure 5 Variation of decomposition temperature with different metal-oxides.

oxides seem to have a minimal effect on the degradation of PEO. For the degradation of PAM and PVA, the trend seems to follow the order: PbO > Co_3O_4 > CuO > ZnO > Al_2O_3 with the highest degradation obtained in presence of PbO while Al_2O_3 seems to have minimal effect on the degradation of the polymers. The mechanism of degradation of these polymers in the presence of metal oxides is believed to be similar to that in the absence of metal oxides. The presence of metal oxides increases the degradation rates of the polymers. In applications like oil field mining and injection molding, where high temperatures are involved, metal oxide impurities may prove detrimental to the stability of these polymers.

FTIR spectral analysis

The analysis of the residue at the decomposition temperature was done by FTIR. The pyrolysis was carried out in a similar manner, but the heating was stopped at the peak decomposition temperature, held for 5 min, and the residue was quenched in an atmosphere of nitrogen. The residue so obtained was used for FTIR analysis. Because the presence of PbO or Co_3O_4 had the maximum influence on the degradation of the polymer, polymers coated with either of these oxides were analyzed for products with different functional groups obtained after pyrolysis. The FTIR spectra of samples before and after pyrolysis are shown in Figure 6(a)–(c).

The spectra for PEO coated with Co_3O_4 show bands for C—C, C—O stretching in the region 800–1100 cm^{-1}. The wagging and twisting motions of methylene groups are seen between 1200 and 1350 cm^{-1}. C—H bending and stretching is observed at 1471 and 2890 cm^{-1}, respectively. The broad peak at 3468 cm^{-1} is due to bonded OH groups in the chain.

The metal oxide Co_3O_4 alone gives peaks at 560, 660, and 1383 cm^{-1}. The degraded sample shows peaks at 1108, 1445, 1570, and 1692 cm^{-1}. Alcoholic
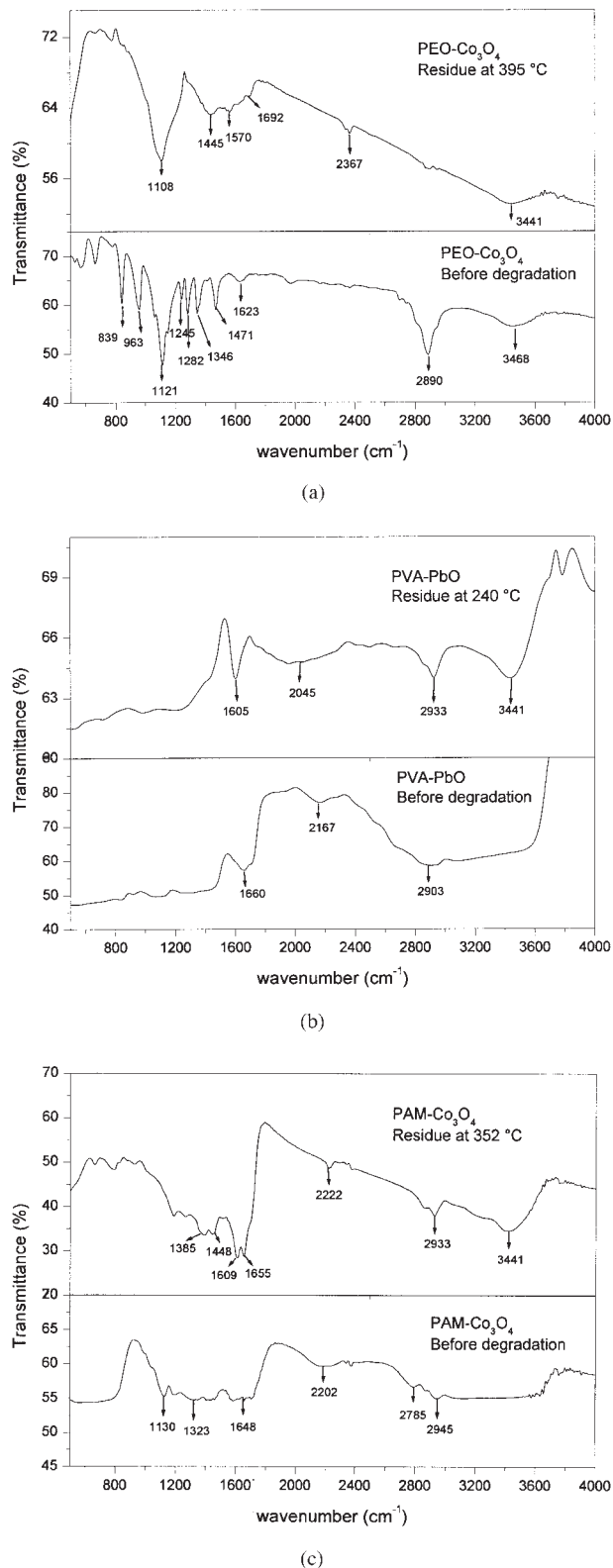

(a)

(b)

(c)

**Figure 6** FTIR spectra of polymer films with metal-oxide: (a) PEO-Co_3O_4, (b) PVA-PbO, (c) PAM-Co_3O_4.

C—C—O stretch occurs between 1050 and 1120 cm^{-1}. Aldehyde and ketonic groups absorb between 1650 and 1750 cm^{-1} depending on saturation, conjugation, etc.

The spectra of PVA coated with PbO show peaks for C—H stretching in CH$_2$ at 2903 cm^{-1}. The peak at 2167 cm^{-1} could correspond to the stretching of terminal C=C—C—H. The broad OH peak between 3200 and 3500 cm^{-1} indicates the presence of bonded hydroxyl groups. PbO gives peaks at 1660 and 1383 cm^{-1}. The degraded sample shows peaks for C=C at 1605 cm^{-1}. A broad peak stretching from 1730 to 2300 cm^{-1} includes weak absorption for carbonyl C=O stretch (because only small amounts are formed) and some amount of alkyne units may also be formed giving rise to absorption at 2045 cm^{-1}. The peak at 2933 cm^{-1} is due to aliphatic C—H stretch and the peak at 3441 cm^{-1} is due to water molecules that are adsorbed or bonded to the polymer chain.

The spectra for PAM coated with Co$_3$O$_4$ show peaks for amide I and amide II bands. The peak at 1425 cm^{-1} is due to C—N stretch. The overlap of C=O stretch and NH$_2$ bending gives amide I and amide II band at 1648 cm^{-1}. Broad amide I bands between 3100 and 3400 cm^{-1} indicate N—H stretch along with bonded O—H stretch. Peak for C—H stretch is also seen at 2940 cm^{-1}. The degraded sample shows peaks corresponding to C—N stretch (1448 cm^{-1}), C=O stretch, N—H bending, formation of new C=C bonds (1609 cm^{-1}), C =N (1655 cm^{-1}), and C(N (2222 cm^{-1}). These are evidences for formation of nitriles and imides. The peak at 3441 cm^{-1} is attributed to bonded OH groups in the degraded polymer chain especially in PEO and PVA. Though PAM does not produce products with bonded OH groups, this peak is observed in the degradation sample of this polymer indicating that it could be also due to strongly adsorbed water molecules.

Miscibility and degradation studies on binary blends

The pyrolysis of binary blends of PEO, PVA, and PAM was investigated at different compositions by dynamic thermogravimetry at a heating rate of 5°C. The miscibility of the blend was analyzed by DSC (Fig. 7) and SEM. The PEO and PVA blend phase-separated even at low mass fractions of either of the component and hence was not investigated for miscibility. The morphology of the films based on the SEM pictures for the blends of PAM with PEO and PVA does not indicate miscibility. To confirm this, DSC of the polymer and their blends was studied. If the polymers are completely miscible, then a single glass transition temperature (that can be determined from Fox equation) in between the glass transition temperatures of the individual polymers should be obtained. The glass
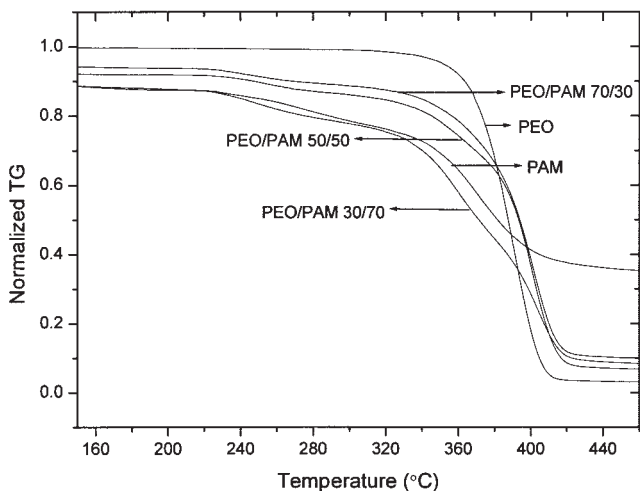

(a)

(b)
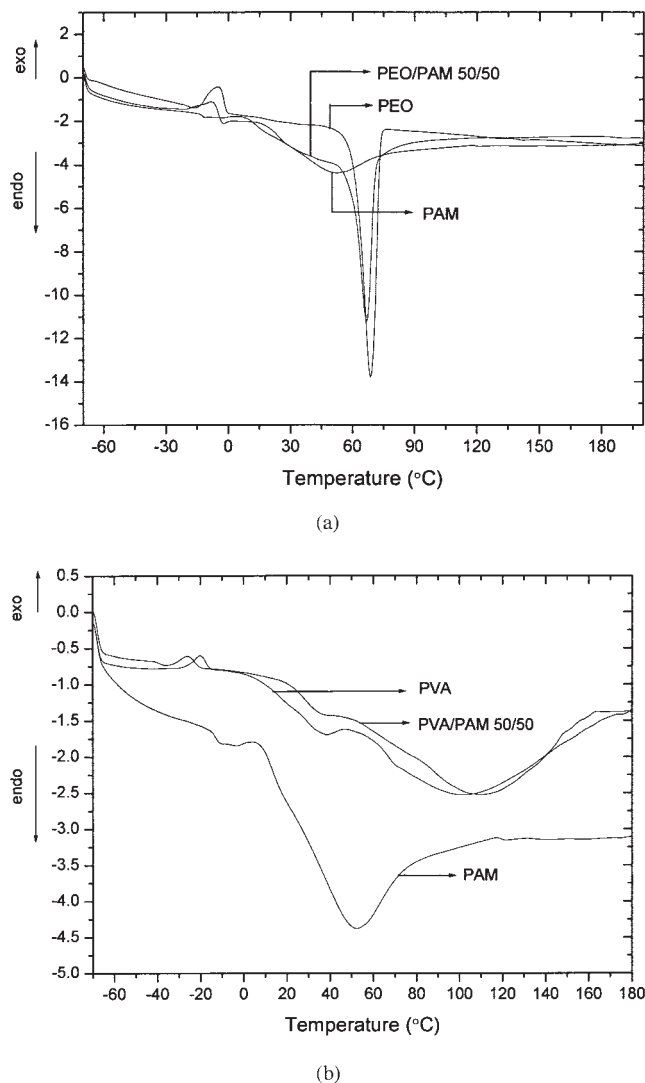
Figure 7 The differential scanning calorimetric endotherms of the blends to determine the miscibility: (a) PEO/PAM, (b) PAM/PVA.

transition temperature reported for PEO is −26°C,[22] which is comparable to that (=−23°C) obtained in this study. The melting temperature of 68°C for PEO is clearly observed. The glass transition temperature of PAM is reported to be between 175 and 200°C,[28] consistent with our observation (on magnification of the DSC plot) of a glass transition temperature of 185°C. For the blend of PAM with PEO, the presence of PAM does not influence the glass transition temperature or the melting temperature of PEO. This indicates that the blend of PAM with PEO is immiscible.
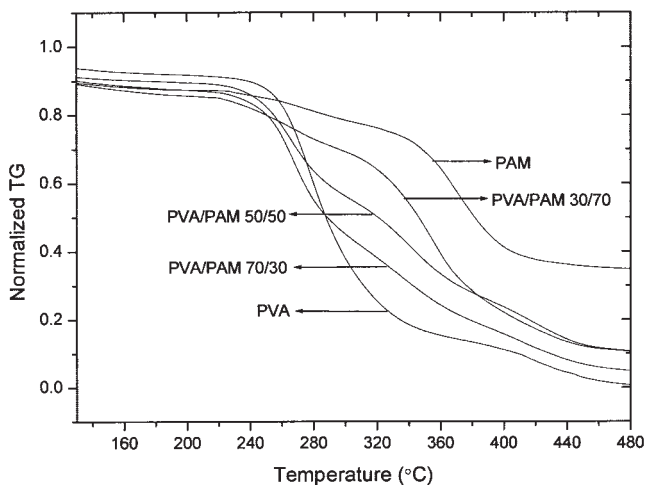
The miscibility of PAM when blended with PVA was examined. The DSC plot for PVA shows a peak at −20°C that can be attributed to the subglass relaxation of PVA associated with local molecular motion.[24] The DSC plot indicates a glass transition temperature of PVA at 75°C, consistent with the value reported in the literature.[22] This glass transi-

tion temperature does not change much in the blend and thus it can be concluded that the blend of PAM and PVA is immiscible.

Polymers in a blend, irrespective of whether they are miscible or immiscible, can interact with each other. The TGA and DTG plots are shown in Figures 8(a) and 9(a). The DTG profile for the blend of PEO with PAM show an overlap of decomposition regions between 320 and 400°C but the peak decomposition temperatures observed in the blend are similar to that obtained for individual polymers. The TG and DTG profiles for the degradation of a binary blend of PVA and PAM are shown in Figures 8(b) and 9(b). The DTG profile shows that the regions of decomposition can be broadly divided in to two regions where the first region of 200–330°C corresponds primarily to the degradation of PVA while the second region of 330–480°C corresponds
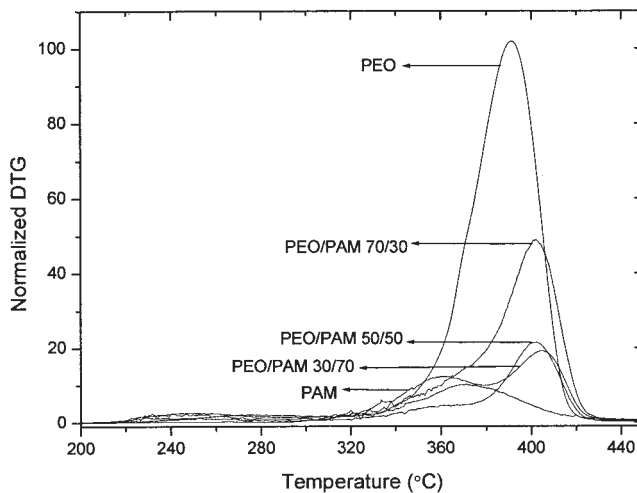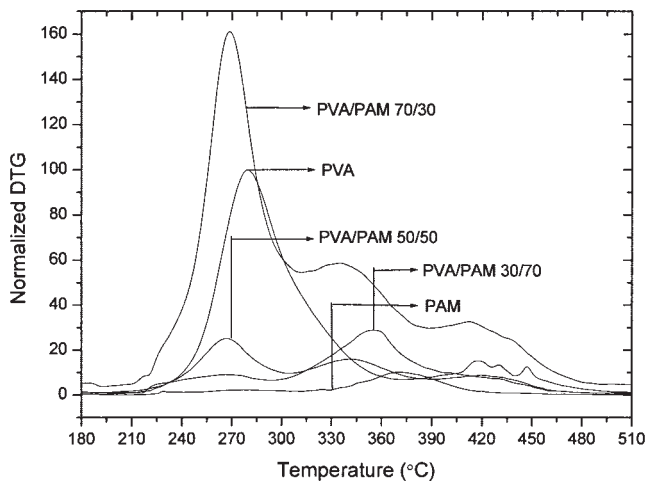

(a)

(b)

Figure 9 Differential thermogravimetric profiles for pure polymers and their binary blends: (a) PEO/PAM, (b) PAM/PVA.


(a)

(b)

Figure 8 Thermogravimetric profiles for pure polymers and their binary blends: (a) PEO/PAM, (b) PAM/PVA.

primarily to the degradation of PAM. A simple additive rule can be used to determine the interaction of the binary blends,[29] where the contributions from each polymer in the blend is calculated using the equation, $(DTG)_{total} = \sum_{i=1}^{2} x_i (DTG)_i$, where i refers to the ith mass fraction of the polymer in the blend and x_i refers to the weight fraction of one polymer in the blend and $(DTG)_{total}$ refers to the mass loss calculated. Figure 10 demonstrates the interaction behavior in the blends where the points are experimental data for the PVA–PAM blend while the solid straight lines represent the case where there is no interaction between the polymers. Because only a slight deviation from linearity is observed, it can be concluded that the polymers do not interact with each other. Further, the DSC endotherms indicate immiscibility of the polymers in the blend.
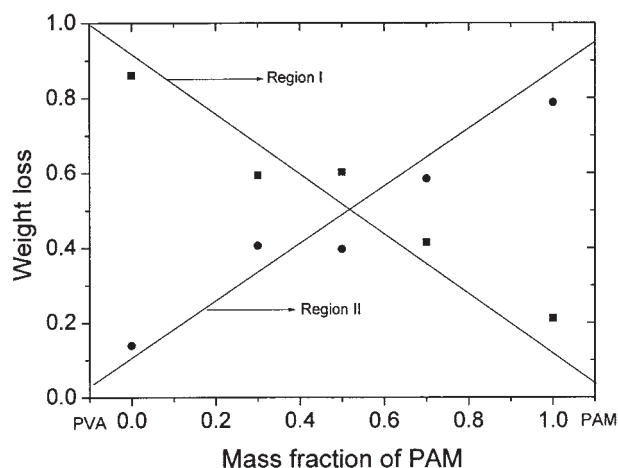
Figure 10 The variation of the weight loss with the mass fraction of PAM in the PVA–PAM blend.

CONCLUSIONS

The effect of five different metal oxides namely PbO, Co_3O_4, CuO, ZnO, and Al_2O_3 on the thermal degradation of poly(ethylene oxide), polyacrylamide, and poly(vinyl alcohol) was investigated. While the metal oxide did not influence the degradation of PEO, it significantly influenced the degradation rates of PAM and PVA. The decomposition temperature of PVA coated with PbO was decreased from 270 to 239°C. Similarly for PAM the decomposition temperature decreased from 370°C to 352°C. Thus the thermal stability of PAM and PVA is reduced in the presence of metal oxides. To determine the interaction of the polymers, the miscibility of binary blends was investigated. Since the blend of PEO–PVA phase separated even at low mass fractions of either polymer, the miscibility and thermal degradation of PEO–PAM and PVA–PAM was investigated. These blends were found to be immiscible and there was no interaction between these polymers during the thermal degradation.

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