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Preparation, characterization, and thermal studies of γ-Fe_2O_3 and CuO dispersed polycarbonate nanocomposites

Arunkumar Lagashetty · H. Vijayanand ·
S. Basavaraja · Mahesh D. Bedre · A. Venkataraman

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Abstract Polycarbonate with γ-Fe_2O_3 and CuO dispersions were carried out by solvent casting method to make polycarbonate-γ-Fe_2O_3 and polycarbonate-CuO composite films. These films were characterized for the molecular structure through FTIR spectroscopy and crystallinity by X-ray diffraction (XRD) measurements. The morphology of polycarbonate-γ-Fe_2O_3 was found to be different from that of polycarbonate-CuO composite films based on the scanning electron micrograph (SEM) images. The thermal traces of composites are different from that of pure polycarbonate which indicating the catalytic decomposition when compared with virgin polymer which is oxidative decomposition. An understanding of the structure, morphology, and thermal behaviour of the composite films are envisaged in the present study.

Keywords Characterization techniques · Nanocomposite · Polycarbonate · Thermal study

Introduction

Flurry of research activity has occurred in producing polymer composites and nanocomposites by incorporating inorganic nanoparticles [1]. The unique properties of nanoparticles are due to quantum-confinement or surface effects that become operative on the nanoscale [2]. Polymer nanocomposite materials represent a new alternative to conventionally used nanoscopic inorganic material-filled polymers. Because of their nanometer sizes, filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites [3, 4]. These include increased modulus and strength; outstanding barrier; properties that improved solvent and heat resistance, and decreased flammability. Researchers have attempted to enhance the desired properties of polymer nanocomposites and, thus, to extend their utility by reinforcing them with nanoscale materials to drive improved properties compared with the more conventional particulate-filled microcomposites [5, 6].

In order to improve the properties of the polymer, nanoscopic inorganic materials typically 10–100 nm are dispersed in an organic polymer matrix constituting polymeric nanocomposite [7]. Nanocomposite materials based on nanosized inorganic materials have been of great interest to researchers due to their applications [8]. Metal oxides dispersed polymer nanocomposites have been extensively studied, since they exhibit interesting properties with many applications such as quantum electronic devices, magnetic recording materials, sensors, capacitors, smart windows, toners in photocopying, conducting paints, and rechargeable batteries [9–13]. These composites were often prepared by dispersing nanomaterials in a non-conducting polymer matrix [14]. Looking into the wide application of these, in this study, we have prepared polycarbonate nanocomposite films by dispersing CuO and γ-Fe_2O_3 material in the polycarbonate matrix through solvent casting method. The as-prepared films were characterized by characterization techniques, and thermal studies were undertaken to study the effect of doping

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A. Lagashetty
Appa Institute of Engineering and Technology,
Gulbarga 585102, India

H. Vijayanand · S. Basavaraja · M. D. Bedre ·
A. Venkataraman (✉)
Materials Chemistry Laboratory, Department of Materials
Science, Gulbarga University, Gulbarga 585106, India
e-mail: raman_chem@rediffmail.com

CuO and γ-Fe_2O_3 inorganic materials into the non-conducting polymer.

Experimental

Synthesis of metal oxide (CuO, γ-Fe_2O_3) dispersed polycarbonate nanocomposite films

Preparation of CuO and γ-Fe_2O_3 nanomaterials were reported in our earlier study [15–17]. Solvent casting method similar to our earlier study [6, 14, 18] was adopted for the synthesis of polycarbonate nanocomposite films and is discussed as below. A known weight of polycarbonate was dissolved in a minimum quantity of dichloromethane as a solvent and the whole solution was then transferred to vacuum rotary evaporator. Known quantities of prepared metal oxides (CuO, γ-Fe_2O_3) individually were sonicated for 0.5 h in a separate container. The above sonicated metal oxides were then individually mixed with polycarbonate solution in a rotary evaporator which was constantly maintained at 353–363 K in water bath. The solvent was then evaporated from the rotary evaporator slowly by applying the vacuum with a rotation of 200 rpm/min, uniformly dispersed metal oxide polycarbonate films were obtained, and these are designated as PC/γ-Fe_2O_3 and PC/CuO for Polycarbonate-γ-Fe_2O_3 and Polycarbonate-CuO nanocomposites, respectively. These as-prepared films are free from air bubbles.

Characterization

The powder X-ray diffraction patterns for the films were obtained from GEOL JDX-8P X-ray diffractometer using CoK_α radiation in the 2θ range of 10–90°. The morphology of the polymer as well as polymer nanocomposite films were obtained from Leica Cambridge-440 scanning electron microscope. The infrared spectra of polymer and its metal oxide composites were recorded on a Perkin-Elmer FTIR spectrometer [model 100] in the range 4,000–300 cm^{-1} to understand the metal-oxygen bonding. Thermal traces were obtained from Mettler Toledo Star instruments (Weinheim, Germany) under a dynamic flow of nitrogen at a flow rate of 100 mL min^{-1} and at a heating rate (V_h) of 283 K min^{-1}.

Results and discussion

X-ray diffraction (XRD) studies

Figure 1a, b shows the XRD pattern of PC/γ-Fe_2O_3 and PC/CuO composite films, respectively. The sharp intensity peaks were found in the polycarbonate nanocomposite films show the development of crystallinity in the PC matrix. Inserted CuO and γ-Fe_2O_3 nanoparticles peaks are indexed in the composite patterns. The shift in (311) and (320) peaks in PC-γ-Fe_2O_3 pattern also reflect the composite formation. Developed crystallinity in PC was due to the complexation of γ-Fe_2O_3 and CuO nanomaterials with polycarbonate matrix. XRD patterns of pure CuO and γ-Fe_2O_3 nanoparticles reported earlier show high crystallinity [16, 17]. A comparison of the X-ray diffraction pattern of pure CuO and γ-Fe_2O_3 with its polycarbonate nanocomposites shows that the diffraction peaks observed were less intense and broad. This nature of the pattern suggests a decrease in the degree of crystallinity of CuO and γ-Fe_2O_3 at higher concentrations and dominant presence of the amorphous phase of PC. The broad halos in the region 5–20° correspond to the organic phase present in the PC sample. Furthermore, the existence of the amorphous phase of γ-Fe_2O_3 and CuO observed in the composite was due to surface coating of the PC during the complexation.

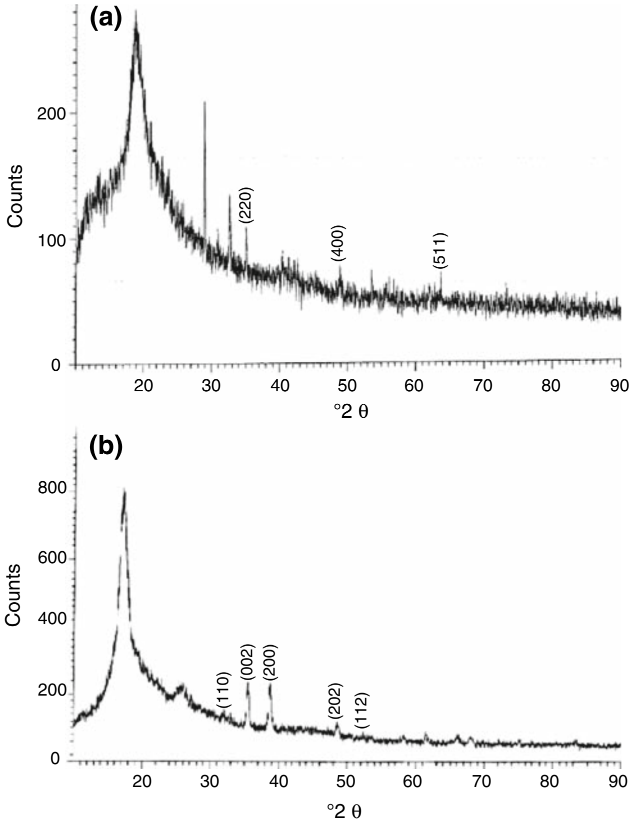

Fig. 1 XRD pattern of (**a**) PC/γ-Fe_2O_3 (**b**) PC/CuO nanocomposite

Scanning electron micrograph (SEM) studies

Figure 2a, b shows the SEM image of PC with low and high magnification, respectively. The image is observed as an amorphous sheet-like structure under high magnification. Some nanosized particles on homogenous polycarbonate film are observed with different shapes.

Figure 3a, b shows the SEM images of PC/γ-Fe_2O_3 composite with low and high magnification, respectively. The amorphous nature of PC now looks changed with well-dispersed, nanosized γ-Fe_2O_3 on the PC matrix. Under high magnification, the nanosized γ-Fe_2O_3 particles look as agglomerates of different shapes and sizes. XRD pattern also shows the crystalline nature of this composite.

Figure 4a, b shows the SEM image of PC/CuO composite at low and high magnification, respectively. Under low magnification, the continuous and very well-dispersed CuO particles on the polymer matrix were seen, changing the amorphous nature of the PC matrix to a partially crystalline dense form. On higher magnification, we observe the close knitting of the CuO nanoparticles to form continuous chains, indicating a self-assembled, close-knitted chain of nanosized CuO. These results were well supported from XRD results by showing the crystalline peaks in the composite (PC/CuO).

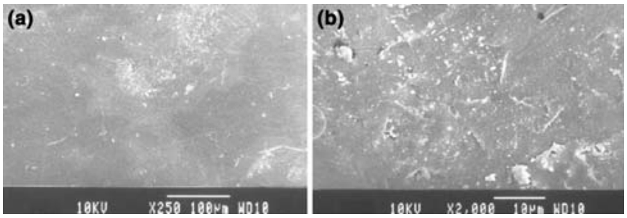

Fig. 2 SEM image of PC at (**a**) low magnification and (**b**) high magnifications

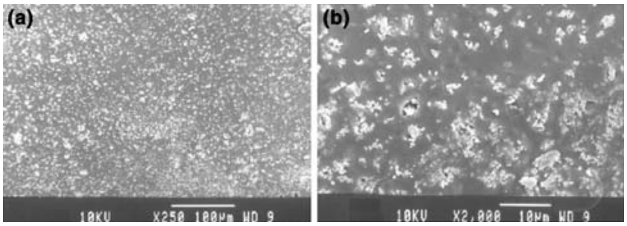

Fig. 3 SEM image of PC/γ-Fe_2O_3 at (**a**) low magnification and (**b**) high magnification

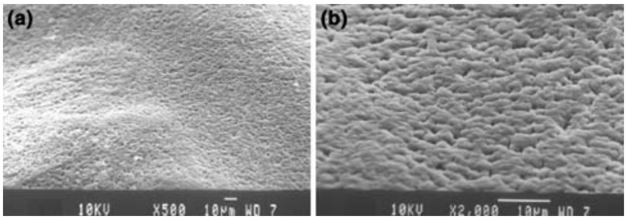

Fig. 4 SEM image of PC/CuO at (**a**) low magnification (**b**) high magnification

Fourier transform infrared (FTIR) spectroscopy studies

Figure 5a, b shows IR spectra of PC and PC/γ-Fe_2O_3, respectively. On comparison of these spectra, the presence of bands at 445, 550, and 1,082 cm^{-1} (Fig. 5b) in the PC/γ-Fe_2O_3 were of γ-Fe_2O_3 in the polymer matrix, although some additional peaks and shift in vibrational frequency were also observed. These additional peaks and shifts in the PC composite spectrum were due to possible hydrogen bonding and interactions between metal oxide and PC [19].

Thermal analysis studies

Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) of PC and PC/γ-Fe_2O_3 were undertaken. Figure 6a, b shows TG/DTA trace of PC and its γ-Fe_2O_3 composite, respectively. The TG trace shows a two-step mass loss [20]. The first mass loss of 46% was observed from 683 to 733 K. The mass loss in this region was fast and indicates a partial decomposition of the surface-oxygenated PC. The second mass loss of 34% occurs

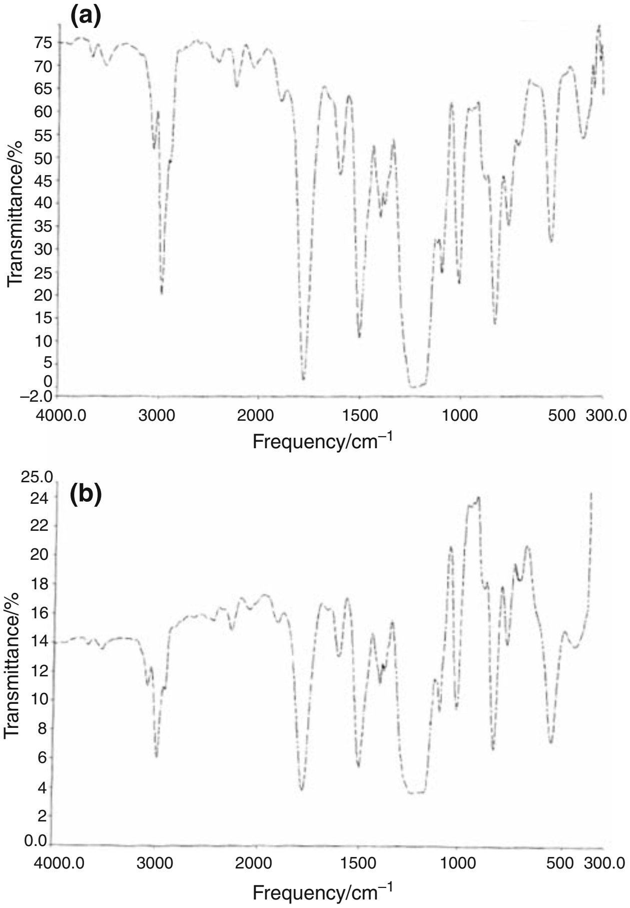

Fig. 5 FTIR spectra of (**a**) pure PC and (**b**) PC/γ-Fe_2O_3 composite

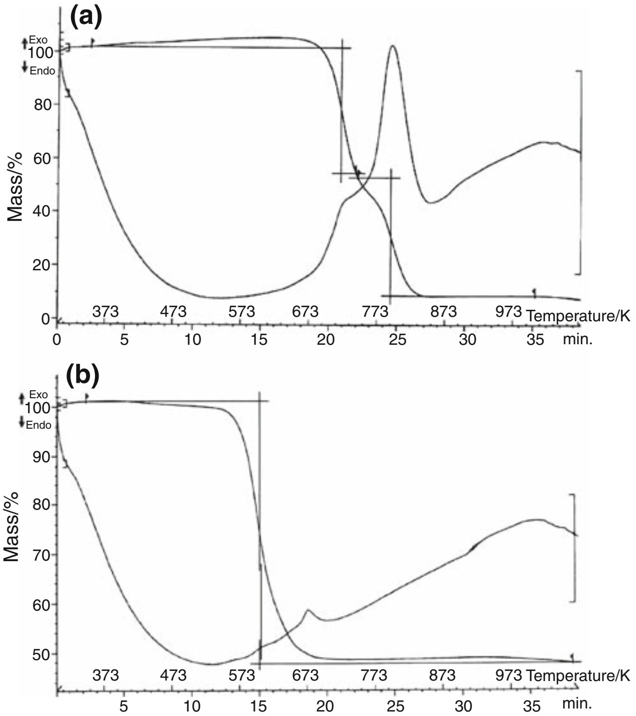

Fig. 6 TG/DTA trace of (**a**) pure PC and (**b**) PC/γ-Fe_2O_3 composite

in the range from 733 to 833 K was rather slow. The partially decomposed PC now gets completely decomposed leaving behind a residual char of mass 10% [21]. An interesting feature of TG trace of PC shows an increase in mass with increase in temperature from 383 to 673 K. This was due to adsorption of oxygen on the PC matrix to form a surface-oxygenated PC, which is also in concurrence with the broad peak observed in DTA trace centered at around 533 K. The DTA trace shows an exothermic peak at 793 K with a shoulder at 713 K corresponding to the complete decomposition of PC. The DTA trace was in concurrence with the mass loss of the two-step decomposition process observed in the TG trace.

The thermal trace of the composite is interesting. There was no total increase in mass of the composite when compared with the virgin polymer. This nature clearly indicates that the γ-Fe_2O_3 in the composite inhibits the surface oxidation of the PC (Fig. 6a, b). The first mass loss of 2% from 433 to 553 K indicates the loss of H_2O from the γ-Fe_2O_3 of the sample. The second mass loss of 50% occurs from 553 to 693 K. This decomposition was also smooth and progressive, indicating a defined pathway. This nature of the thermal trace suggests that γ-Fe_2O_3 also acts as catalyst in the decomposition of the PC. The increase in the percentage of residue when compared with PC may be due to the formation of iron carbide and carbon. DTA trace shows a small exothermic peak at around 683 K corresponding to decomposition of PC.

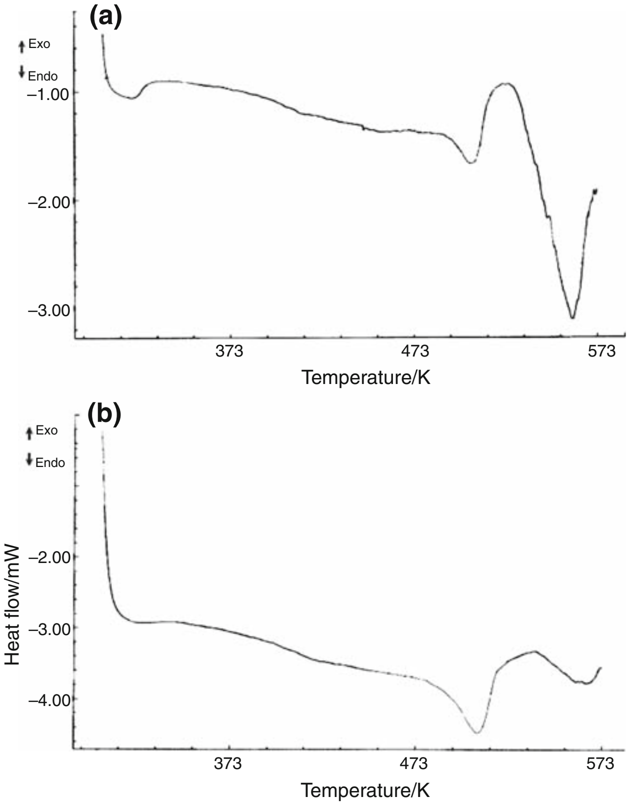

Fig. 7 DSC trace of (**a**) PC/γ-Fe_2O_3 (**b**) PC/CuO composite

Figure 7a shows the results of DSC trace of PC/γ-Fe_2O_3 composite. Here, one observes the similar nature of the TG trace; however, the peaks are more pronounced when compared with the DTA trace (Fig. 6b). The two endo peaks observed at 693 and 563 K were of decomposition process, which was also evident from a broad peak in DTA trace (Fig. 6b). The interesting part of the γ-Fe_2O_3 composite was the nature of the decomposition, which from the DTA and the DSC trace shows endothermic peaks suggesting that a catalytic decomposition rather than the oxidative decomposition has taken place. In order to understand, further, we report the DSC trace of PC/CuO composite in Fig. 7b. Herein also, two endo peaks at 508 and 573 K were observed, clearly suggesting the catalytic decomposition of the composite. Hence, we may, with caution, suggest that an internal thermal behavior has occurred in nanocomposites when compared with the virgin polymer. The oxidative decomposition is converted to catalytic decomposition for the composites [22].

Conclusions

The addition of metal oxides into the polymer matrix results in the decrease in degree of crystallinity of metal oxides and increase in degree of crystallinity of polymer to some extent. These results confirm the formation of polycarbonate nanocomposites. Morphological study represents the change in morphology with addition of nanoscopic inorganic materials to polymers. Infrared study reveals that additional reflections and shift in frequency were observed in polymer composite materials when compared to its pure polymer. From the thermal study, an increase in the thermal stability of the filled polymers, as well as the catalytic behavior of the metal oxides decomposition, were observed.

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