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Preparation and Thermal Properties of Poly(isobornyl methacrylate)/Graphite Composites

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This study reports the synthesis and thermal properties of poly(isobornyl methacrylate)/graphite composites. Homopolymer of isobornyl methacrylate was synthesized by free radical polymerization using benzoyl peroxide as an initiator at 65 ^{o}C. Poly(isobornyl methacrylate) composites were successfully prepared with graphite (G) in various ratios *via* solvent casting technique. Structures of the homopolymer and their corresponding composites were analyzed by Fourier transform infrared (FT-IR). TGA/DTA simultaneous system was used to determine the thermal behavior of the prepared materials. Differential Thermal Analysis (DTA) measurements showed that Tg values of the composites were lower than that of homopolymer. Thermal stability of the polymer composites increased with increasing the amount of graphite added to homopolymer.

Keywords: *Poly(isobornyl methacrylate), graphite, composite, thermal properties*

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1. Introduction

Acrylate and methacrylate polymers have played an important role to develop materials that are compatible with dental fillings, soft tissues, and orthopedic applications [1-3]. Vinyl esters activated by acrylate/methacrylate were immediately polymerized. In this process, free radical polymerization method was used to form linear, branched and network polymers. The hydrophobic and hydrophilic balance, type of charge and concentration inside the polymer can be tunes by simple co-polymerization of acrylate/methacrylate monomers having distinctive substituents. Acrylic and methacrylic homopolymers have many properties. They are highly transparent, chemically stable, optically clear, and able to adhere in addition to enhanced mechanical properties [4-8]. They are utilized to make progressive composites with a balance of advanced processing and performance. Carbon nano-tubes [9,10], graphite [11, 12] or carbon black [13-15] are members of an important research area when these composites are used as fillers. Thermal degradation activity of polymeric compounds is motivating and useful to characterize. Thus, thermogravimetric analysis (TGA) is used, as it is very simple. It easily describes thermal degradation behavior and kinetic parameters to reflect useful info [16-17]. Recent work in composite science and technology has shown that combining these two moieties in polymers i.e. carbon nanotubes and graphite can enhance their electrical conductivity up to many folds; without compromising the mechanical and other important physicochemical properties [18].

In this study, isobornyl methacrylate homopolymer (poly(IBMA)) and composites prepared with graphite in different ratios were used. Composite studies using poly(isobornyl methacrylate) as a matrix are very few. This study was aimed to explore the morphological effects of graphite material in the composite, and thermal properties of poly(IBMA)/G compounds in an integrated manner. It was also aimed to investigate the structural and morphological properties of pure homopolymer and corresponding compounds.

2. Experimental

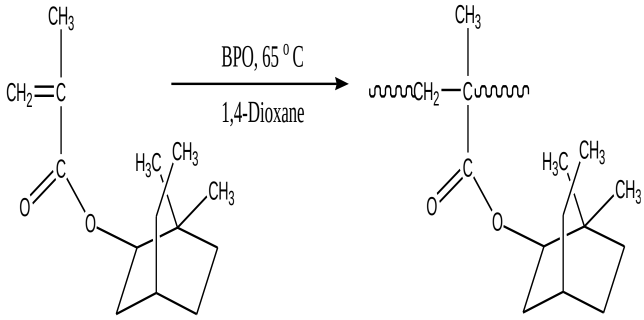
2.1. Materials and characterization techniques

Isobornyl methacrylate was purchased from Sigma-Aldrich. 1,4-Dioxane and dichloromethane were of analytical grade. Benzoyl peroxide (BPO), used as the initiator, was recrystallized from chloroform– methanol (1:1) mixture and dried under vacuum. Graphite was purchased from Sigma Aldrich.

Infrared spectra were obtained with a Perkin–Elmer Spectrum One FT-IR system and recorded using universal ATR sampling accessory within the wavelength range of 4000–650 cm^{-1}. Thermal stabilities and the glass transition temperatures of the polymers were investigated on a Perkin–Elmer TGA/DTA 7300 thermal analysis systems, under nitrogen flow with a heating rate of 20 °C/min. The powder morphology of composites was performed using ZEISS & EVO LS 10 Scanning Electron Microscopy (SEM).

2.2. Preparation of poly(IBMA) and poly(IBMA)/graphite composites

Homopolymerization of IBMA was carried at 65 ^{o}C in the presence of 1,4-dioxane using BPO (1 % wt/wt of the monomer) as the initiator. About 1 g of the monomer and BPO were dissolved in 1,4-dioxane (5 mL) in a polymerization tube. The mixture was degassed by passing high pure argon. Polymerization was performed at 65 ^{o}C in a thermostatic oil bath. After 12 hours, polymerization mixture was cooled 25 ^{o}C. Homopolymer was precipitated in excess ethanol and filtered. The precipitated polymer was purified by repeated reprecipitation from dichloromethane solution using ethanol and dried under vacuum at 40 ^{o}C for 24 h. The structure of synthesized poly(IBMA) is given in Scheme 1.



Scheme 1. Synthesis of poly(IBMA)

Composites were fabricated in three steps. In the first step, amounts of graphite (1 and 5 % wt/wt) were shaken in the Bandelin Ultrasonic Homogenizer Sonicator processor in dichloromethane for 3 hours to allow an appropriate dispersion of graphite. In the second step, isobornyl methacrylate homopolymer was dissolved in dichloromethane. In the third step, the dichloromethane solution of poly(IBMA) was added to dispersed graphite in the dichloromethane. The mixture was vigorously shaken for 5 hours till the graphite uniformly dispersed in the polymer matrix. Composites were formed *via* solvent casting technique. After evaporation of the solvent, homogeneous composites were obtained that were dried in a vacuum oven at 40 °C for 24 h. Thermal and morphological properties of composites were investigated. Composites were compared in terms of the amount of polymer-doped filler.

3. Results and Discussion

3.1. Characterization of Composites

FTIR spectra of poly(isobornyl methacrylate) and their composites are shown in Figure 1. A band at 2953 and 2880 cm^{-1} was observed that belongs to the methyl and methylene groups. There are vibrational bands at 1729 cm^{-1}, which corresponds to the C = O stretching vibration of the isobornyl methacrylate ester group. In the FTIR spectrum of isobornyl methacrylate monomer, a distinct vibrational band is visible at 1640 cm^{-1} (the stretching vibration band of the C = C bond), that disappeared in the FTIR spectrum of poly(IBMA). This confirmed that the double bond of isobornyl methacrylate underwent chemical reaction. The symmetrical bending vibrations of methyl groups are clearly observed at 1473 and 1452 cm^{-1}. The band at 1147 cm^{-1} corresponds to the C-O stretching. When graphite is added to the polymer, these bands generally do not change.

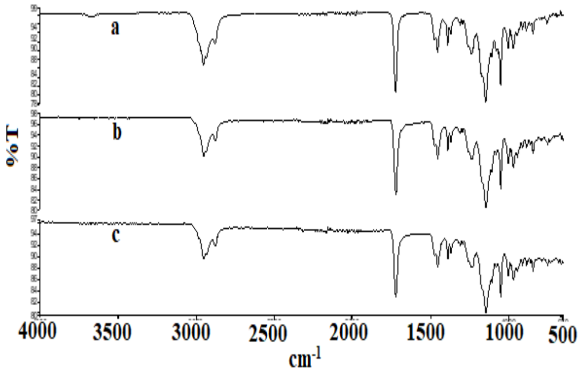


Fig. 1. FT-IR Spectrum of a-) poly(IBMA) b-) poly(IBMA) / %1 G c-) poly(IBMA) / %5 G

3.2. SEM micrography analysis of poly(IBMA)/ graphite

The morphology of graphite filled poly isobornyl methacrylate composites {poly(IBMA)/%5G} were examined by using a scanning electron microscope. Figure 2 show variously magnified SEM images of the poly(IBMA)/%5G composite. The samples were gold-sputtered prior to measurements. The surface of amorphous structured pure poly(IBMA) was smooth with few cracks. The graphite particles were big in size in the composite. A very high magnification of SEM images shows the uniform dispersion of graphite in the polymer; thus both are compatible to each other.

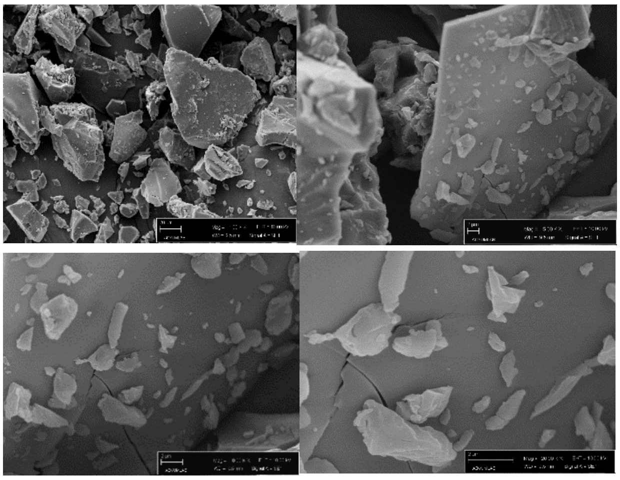


Fig. 2. SEM images of poly(IBMA) / %5 G a-) with 5.00 KX magnification b) with 10.00 KX magnification, c) with 20.00 KX magnification, d) with 40.00 KX magnification

3.3. Glass Transition Temperature

Differential Thermal Analysis (DTA) was performed to determine the glass transition temperatures (Tg) of homopolymer and its corresponding composites. Tg measurements were performed at 20 °C/min under nitrogen atmosphere (Table 1). Figure 3 show the DTA thermograms for one homopolymer and two graphite filled composites. Tg values of poly(IBMA), poly(IBMA)/%1G and poly(IBMA)/%5G were 206, 202 and 198 °C, respectively. Tg values of the composites were lower (Figure 3) than the those of the homopolymer. The reason may attributed to the fact that the graphite particles in the polymer reduce the mobility of the chain.

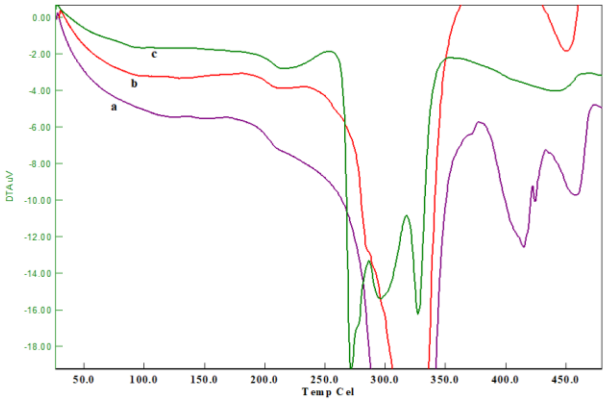


Fig. 3. DTA curves of a-) poly(IBMA) b-) poly(IBMA) / %1 G c-) poly(IBMA) / %5 G

3.4. Thermogravimetric Analysis

Thermal stabilities of homopolymer and its composites were determined by thermo-gravimetric analysis under nitrogen atmosphere at a 20 °C/min heating rate. TGA measurements were carried out using about 5-8 mg samples. TGA curves of homopolymer and its composites are shown in Figure 4. Thermograms clearly indicate that poly(isobornyl methacrylate) underwent one-step decomposition while composites went through two-step. Thermal behavior of any polymer is significantly affected by the incorporation of a filler into the polymer chain. Thus, it is important to investigate the thermal behavior of the prepared composites.

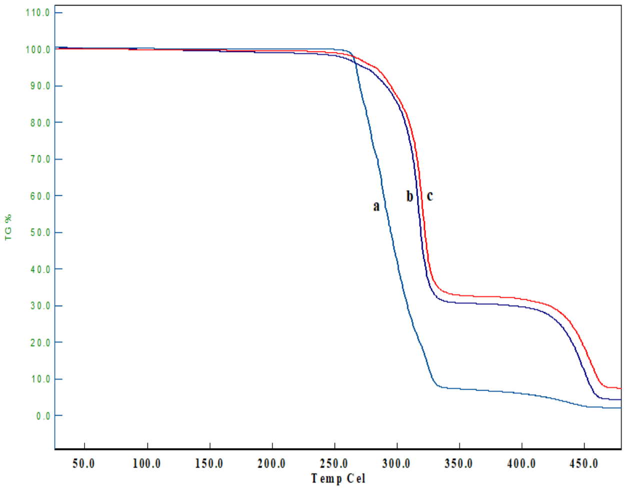


Fig. 4. TGA curves of a-) poly(IBMA)
b-) poly(IBMA) / %1 G c-) poly(IBMA) / %5 G

Thermal decomposition process of composites occurred after homopolymer. This behavior showed that the graphite particles increased the thermal stability of polymer composites. Also, it has been reported that the strong interfacial interactions between the polymer matrix and fillers may increase thermal stabilities. The raising thermal stability of the composites with respect to the homopolymer can be assigned to the segmental mobility of the polymer chains, depending on the surface of the graphite particles. Certain degradation characteristics of the polymer and its composites are compared in Table 1.

Table 1. TGA results of the homopolymer and its composites

T_{max}: maximum decomposition temperature

Polymer	Tg	T_{max}	%50 Weight Loss	% Residue
Poly(IBMA)	206	295	295	2
Poly(IBMA) / %1 G	202	308;470	319	4
Poly(IBMA) / %5 G	198	312;485	323	8

4. Conclusions

In this study, isobornyl methacrylate homopolymer was synthesized by free radical polymerization method. Composites of these homopolymer were prepared by solution casting with graphite in different percentages. The structure and characterization of synthesized composites were ascertained by FT-IR, SEM, and TGA/DTA. SEM micrographs confirmed the uniform distribution of graphite into homopolymer matrices. Differential thermal analysis has indicated that Tg of composites decreased with the addition of graphite into the polymer. Differential thermogravimetric analysis has revealed that poly(IBMA) / graphite composites have underwent to the double step decomposition whereas poly(IBMA) has only passed through single step decomposition. The thermal stability of the composites has increased with the addition of graphite to the polymer.

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