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Synthesis and thermal degradation kinetics of poly(benzyl methacrylate)/graphite composites

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In this work, poly(benzyl methacrylate) poly(BzMA) was synthesized by free radical polymerization in 1,4-dioxane solution at 70 °C, using 2,2'-Azobisisobutyronitrile (AIBN) as initiator. Poly(benzyl methacrylate)/graphite (poly(BzMA)/G) composites were successfully prepared in various ratios of graphite *via* solvent casting technique. The structural properties of the composites were analyzed by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). DTA measurements showed that the Tg values of the composites were lower than the Tg value of the homopolymer. Thermal stability of the polymer decreased when the amount of graphite in the polymer is increased. The average of activation energy of poly(BzMA)/G 5% *via* FWO method was calculated as 182.7 kJ/mol.

Keywords: *Polymer composites, methacrylate, graphite, thermal decomposition, activation energy*

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1. Introduction

Aromatic acrylate and methacrylate monomers and their corresponding polymers are become popular these days [1–3]. The presence of aromatic rings make them more attractive to the to the polymers due to their supramolecular properties like pi-pi staking, partial dipoles etc. They comprise an important class of polymers [4–6]. Poly(phenyl methacrylates) are thermally stable that increases their demand for industrial and commercial usage [7,8]. There are various types of aromatic acrylates where phenyl and benzyl methacrylate are very prevalent methacrylate esters [9]. Due to their functionalities, these types of polymers are appropriate for different biomedical applications e.g., genes, drugs, protein transport etc. [10, 11]. Poly(benzyl methacrylate) is widely utilized in the dye industry, orthodontic adhesive compositions, transparent adhesives, inkjet inks, and nanoprinting lithography [12-14]. They are also used as a stationary phase in liquid chromatography. Because of its hygroscopicity, BzMA are being utilized in processes where high pressure and solid-liquid-vapor phase systems are developed. In addition, they are used in the morphology of microtubes and in color filter photoresistors. Thus, it is important to understand the molecular structural data of methacrylate monomers on the basis of these polymers.

Polymer composites can be categorized as multifunctional materials due to their physical and chemical properties [15-16]. Because they are biocompatible, biodegradable, renewable and inexpensive, they are applied in many industrial applications. Organic or inorganic polymeric materials are electrical insulators, which limits their use as

smart materials in electrically conductive application. Attempts to move from insulation to conductive polymer composites raise nano-carbon filler-like carbon nano-tubes [17], nano-fibers [18] and graphene [19]. Brilliant thermal, mechanical, and electrical properties of composite materials [20] opens new research areas in polymer matrix composites (PMC). They are lightweight, inexpensive, corrosion resistant technologies that offer a wide range of electrical conductivities.

Scientific literature is limited regarding graphite-containing composites of poly benzyl methacrylate. Therefore, in this study, composites of poly benzyl methacrylate with graphite were prepared at different ratios. It was aimed to investigate the effect of graphite on thermal properties of poly(BzMA), structure and thermal degradation kinetic of pure homopolymer and its composites

2. Experimental

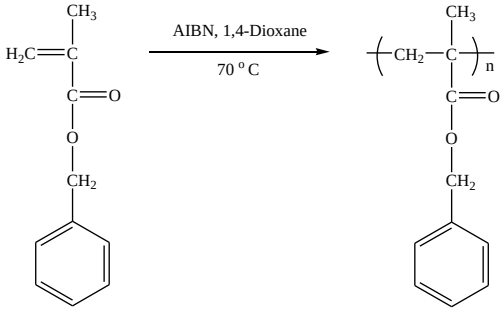
2.1. Materials and Instrumentation

Benzyl methacrylate was purchased from Sigma-Aldrich. 1,4-Dioxane and dichloromethane were used as received. AIBN (2,2-azobisisobutyronitrile), the reaction initiator, was purified by recrystallization and dried *in vacu*. Graphite was purchased from Sigma Aldrich.

Fourier Transform Infrared (FT-IR) spectra were recorded using Perkin Elmer Spectrum 100. Thermal stabilities, glass transition temperatures of polymer and composites were investigated on a Perkin Elmer TGA / DTA 7300 thermal analysis systems under nitrogen flow with a heating rate of 20 °C/min.

2.2. Preparation of P(BzMA) and P(BzMA)/graphite composites

Free radical polymerization method was used to prepare the homopolymer of benzyl methacrylate. Polymerization of BzMA was carried out in 1,4-dioxane solvent using AIBN as an initiator at 70 °C. After 12 h, the polymer was cooled at 25 °C. Homopolymer was precipitated in excess ethanol and was dried *in vacu* at 40 °C for 24 h. The structure of P(BzMA) synthesized is provided in Scheme 1.



Scheme 1. Synthesis of poly(BzMA)

Target composites were produced in three steps. In the first step, 1 and 5% graphite (by weight based on the amount of polymer) was dispersed into separate beakers and mixed in a Bandelin Ultrasonic Homogenizer Sonicator for approx. 3 hours for the graphite to properly disperse in the dichloromethane solvent. In the second step, the poly(benzyl methacrylate) was dissolved in dichloromethane, while the solution prepared in the third step was added to the graphite dispersed in dichloromethane.

The mixture was vigorously stirred for 5 hours until it was homogeneously dispersed in the graphite polymer matrix. Composites are formed by solvent casting technique. Homogeneous composites were obtained after evaporation of the solvent, which was dried in a vacuum oven at 40 °C for 24 hours. The thermal properties of the composites were investigated. These composites were compared in terms of the amount of polymer added filler.

3. Results and Discussion

3.1. Characterization of Composites

The FTIR spectra of poly(benzyl methacrylate) and its composites are shown in Figure 1. C-H stretching band of aromatic system was observed at 3092-3058 cm^{-1}. There are symmetrical and asymmetrical stretching bands at 2941 and 2884 cm^{-1}, which belongs to methyl and methylene groups. The band at 1720 cm^{-1} can be attributed to the ester carbonyl stretching vibration of the benzyl methacrylate. Aromatic C=C stretching were observed at 1602, 1495 and 1451 cm^{-1}. In addition, aromatic C-H stretching vibration for mono-substituted benzene was seen at 691 cm^{-1}. When graphite was added to polymer, the stated peaks in general did not show any notable change.

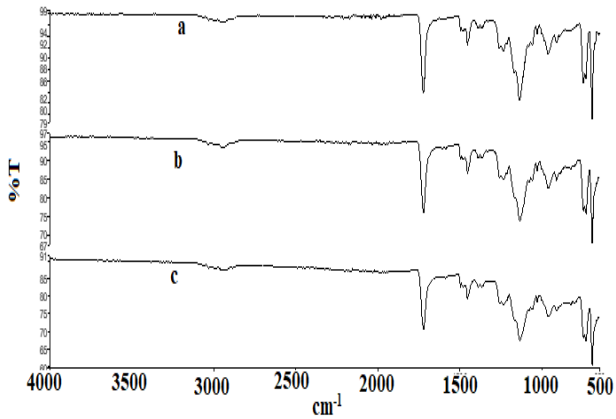


Fig. 1. FT-IR Spectrum of a-) poly(BzMA)
b-) poly(BzMA) / %1 G c-) poly(BzMA) / %5 G

3.2. Thermal Behaviors

Thermal behavior of homopolymer and its composites was examined by differential thermal analysis in the temperature range of 0−200 ºC at 20 ºC/min under N_2 atmosphere. Figure 2 indicates DTA thermograms for one homopolymer and its two composites. The glass transition temperatures (Tg) of poly(BzMA), poly(BzMA) / %1G and poly(BzMA) / %5G were 75, 73 and 72 ◦C, respectively. Tg values of composites showed a single transition. As seen in Figure 2, Tg values of the composites were observed lower than that of the homopolymer. This can be attributed to the fact that the graphite particles in the polymer reduces the mobility of the chain.

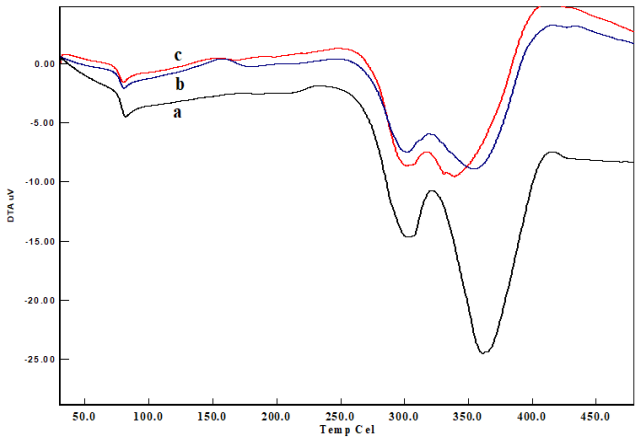


Fig. 2. DTA curves of a-) poly(BzMA) b-) poly(BzMA) / %1G c-) poly(BzMA) / %5G

By introducing a filled in the polymer chain, thermal behavior of a polymer can be altered appreciably. Therefore, it is essential to investigate the thermal behavior of the prepared materials. TGA measurements of homopolymer and its composites were taken under nitrogen atmosphere at 20 º C/min heating rate. Figure 3 shows the thermo-gravimetric (TG) curves of composites compared with that of homopolymer. Whereas poly(BzMA) has presented an initiation temperature at about 209 ºC and two maximum decomposition rates at 305 and 385 ºC, poly(BzMA)/%5 G has shown an initiation temperature of 270 ºC while two maximum decomposition rates at 300 and 345 ºC. For the thermal stability of homopolymer and composites, when the temperatures corresponding to 50 % by weight was taken as a measure, temperatures were observed at 346, 340 and 338 ºC for poly (BzMA), poly(BzMA)/ %1 G and poly(BzMA)/%5 G, respectively. Degradation characteristics of the polymer and its composites are compared in Table 1.

Table 1. Thermal behaviour and decomposition temperatures of the homopolymer and its composites

Polymer	Tg	T_{max}	%50 Weight Loss	% Residue
P(BzMA)	75	305:385	346	0,1
P(BzMA) / %1 G	73	300;345	340	3,1
P(BzMA) / %5 G	72	312;485	338	6,3

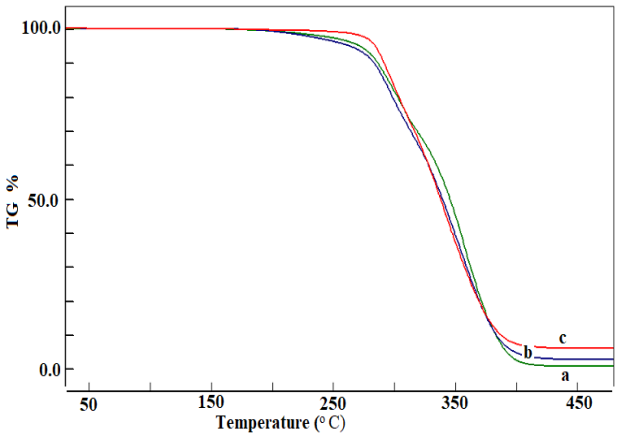


Fig. 3. TGA curves of a-) poly(BzMA) b-) poly(BzMA) / %1G c-) poly(BzMA) / %5G

3.3 Thermal Degradation Kinetics

To study the kinetics of thermal degradation of polymers, isothermal thermogravimetry (ITG) or thermogravimetry (TG) can be selected at different heating rates [21]. ITG is superior to obtain an accurate activation energy for thermal degradation although it has been time-consuming. For the thermal degradation of polymers, where depolymerization is competing with the cyclization or crosslinking due to the side groups, Tg at different heating rates is much more convenient than ITG to investigate the thermal degradation kinetics. Therefore, in this study, TG curves at various heating rates were obtained. The activation energies (ΔE_d) for the thermal degradation of the poly(BzMA) / %5G composite was calculated with Ozawa plots. TG curves measured at various heating rates of poly(BzMA)/ %5G composite are given in Figure 4. Weight loss occurred in the initial stage of both homopolymer and its composites, as discussed earlier. Degradations for the poly(BzMA)/ %5 G was performed in the scanning mode, from 35 to 500 ºC, under a nitrogen flow (20 mL min^{-1}) at the following heating rates: 5, 10, 15 and 20 ºC/ min. Samples of 5-8 mg were held in alumina open crucibles and weight as a function of temperature. The onset temperature of decomposition was increased with increase in the heating

rate. The data was stored in the appropriate built-in program of the processor. The TGA curves were printed at the end of each experiment. The weights of the sample were transferred into a PC at various temperatures.

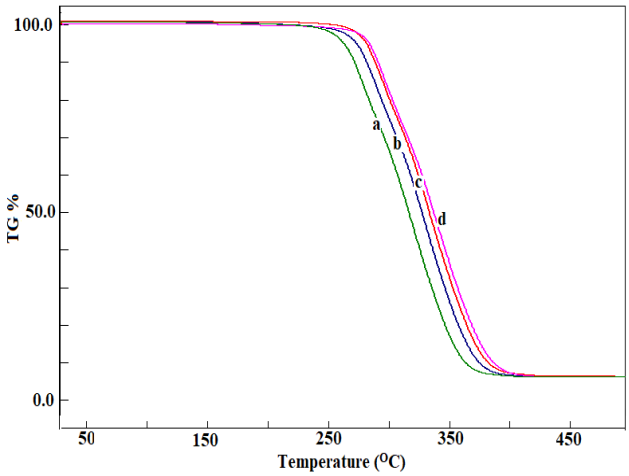


Fig. 4. TGA curves of poly(BzMA) / %5 G for heating rate of a:5 °C/ min b:10 °C/ min; c:15 °C/ min; d:20 °C/ min

According to the method of Flynn-Wall-Ozawa (FWO) [22], the apparent thermal decomposition activation energy, E_d, can be determined from the TGA thermograms under various heating rates as given in equation 1,

$$E_d = -\frac{R}{b}\left[\frac{d \log \beta}{d(1/T)}\right] \qquad \textbf{Equition 1}$$

where R is the gas constant (8.314 J/mol), b is another constant (0.4567) while β is the heating rate (°C/ min).

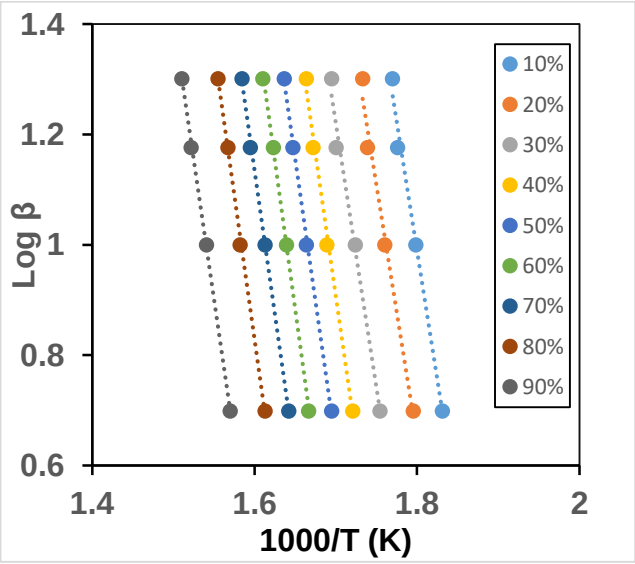


Fig. 5. Determination of the activation energy of poly(BzMA) / %5 G for heating rate of a:5 °C/ min b:10 °C/ min; c:15 °C/ min; d:20 °C/ min

According to Equation 1, the activation energy of degradation can be determined from the slope of the linear relationship between log β and the reciprocal of the temperature. E_d was calculated from the FWO method that is superior than those calculated by other methods for complex degradation because it has do not use the reaction order in the calculation of E_d.

Taking into account the conversion range (α) studied, the parallel lines were indicated for the FWO method. The apparent activation energies calculated at various conversions of poly(BzMA)/G 5% composite using FWO method are given in Table 2. As shown in Figure 5, the average of activation energy of poly(BzMA)/G 5% *via* FWO method was calculated as 182.7 kJ/mol.

Table 2. Values of E_d for each conversion for FWO method

Conversion (α)	Activation Energy E_d (kJ/mol)	Correlation Coefficient (R)
0.1	169.71	0.9891
0.2	167.82	0.9872
0.3	174.56	0.9875
0.4	187.02	0.9941
0.5	186.92	0.9986
0.6	195.66	0.9993
0.7	189.11	0.9990
0.8	190.61	0.9986
0.8	183.45	0.9995
Average	182.70	-

4. Conclusions

Free radical solution polymerization technique was used to synthesize poly(benzyl methacrylate) that was further used to synthesize poly(BzMA)/%1G and poly(BzMA))/%5G composites. These composites were made by solvent casting method. The structure and characterization of homopolymer and its composites was determined by FT-IR, TGA and DTA analysis. Differential thermal analysis has indicated that Tg of the composites decreased with the addition of graphite to the polymer. Temperatures for the thermal stability of homopolymer and composites (based on 50% weight loss), were observed as 346, 340 and 338 °C for poly (BzMA), poly(BzMA)/%1G and poly(BzMA)/%5G, respectively. The graphite added to the polymer reduced the thermal stability of the polymer. Flynn-Wall-Ozawa (FWO) method was used to determine the activation energy of poly(BzMA)/%5G. The results showed that an average activation energy of 182.7 kJ/mol for α = 0.1-0.9 of thermal decomposition was observed in case of poly(BzMA)/%5G.

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