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Effect of graphite on thermal degradation kinetics of poly(benzyl methacrylate-co-styrene)

Taner CEBE[1], Gamze BARIM[1*]

[1]Adiyaman University, Faculty of Sciences and Arts, Department of Chemistry, 02040, Adiyaman, Turkey

In this study, poly(benzyl methacrylate0.33-co- styrene) P(BzMA0.33-co-St) copolymer was synthesized by free radical polymerization at 65 ^{0}C in the presence of BPO initiator in 1,4-dioxane solvent. The structure of the copolymer was characterized by FT-IR and ^{1}H-NMR techniques. Composites of the synthesized P(BzMA0.33-co-St) copolymer with graphite at 1 wt%, 5 wt%, and 10 wt% were prepared by a solvent casting technique. A comparative study of the glass transition temperatures and thermal stability of copolymers and composites was carried out using a simultaneous TGA-DTA system. The glass transition temperature of the pure copolymer was determined to be 88 ^{o}C, while the composites' glass transition temperatures were between 82 and 87 ^{o}C. The thermal degradation kinetics of P(BzMA0.33-co-St) copolymer and P(BzMA0.33-co-St)/G 10 wt% composite were investigated and the average activation energies were determined by FWO and KAS methods. While the activation energy of P(BzMA0.33-co-St) copolymer was determined as 148.898 and 146.431 kJ/mol according to FWO and KAS methods, this value was determined as 186.545 and 185.668 kJ/mol for P(BzMA0.33-co-St)/G 10 wt% composite, respectively.

Keywords: *Copolymer, polymer composites, graphite, thermal properties, activation energy.*

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**Corresponding author: gbarim@adiyaman.edu.tr*

1. Introduction

Polymers are used in many areas of both daily life and industry due to their properties. However, for producing materials for a specific purpose, the properties of polymers can sometimes be limited [1-3]. In this case, polymer composites can be used due to their physical and chemical properties. In recent years, polymeric composites prepared by dispersing inorganic fillers in a polymer matrix have attracted the attention of researchers due to their applications in biological, medical and technological fields [4-6]. Polymer composites exhibit different properties due to the properties of both the polymer matrix and the filler. While the polymer matrix forms the basic structure of these composites, the fillers act as elements that modify the properties of the composite. The type, size, concentration and shape of the filler added to the polymer matrix change the properties of the polymer matrix, significantly determining the mechanical, thermal, electrical and chemical properties of the composite material [7-10]. Furthermore, interactions between fillers and the polymer matrix can improve or weaken the performance of the composite. These interactions depend on factors such as the surface properties of the fillers, their bonding capacity with the matrix, and their load-carrying mechanisms [11]. Consequently, when designing a polymer composite, the selection of a polymer matrix and filler material for the desired purpose is of utmost importance

This study investigates the effect of graphite on the thermal properties of poly(benzyl methacrylate-co-styrene) synthesized by free radical polymerization. Styrene polymer

is a substance that we widely use in daily life and is also used in the medical field, especially in the production of implants and devices. It is also widely used in disposable materials such as gloves and vials. Polystyrene is also preferred in producing laboratory equipment such as petri dishes, pipettes, and sterilization trays [12-14]. Properties such as low cost, thermal stability, and light weight make polystyrene suitable for use in these areas. Due to the recent increasing demand for disposable medical supplies, the need for such biomedical polymers continues to grow significantly. In this study, benzyl methacrylate (BzMA) was chosen as the styrene (St) comonomer. PBzMA is a hydrophobic and amorphous polymer with a relatively low glass transition temperature of Tg PBzMA = 54 °C. This is significantly lower than polystyrene (PSt), with a glass transition temperature of Tg PSt = 100 °C. As a result, the polymerization of BzMA with styrene allows the formation of softer and more easily processable copolymeric structures. PBzMA has numerous potential applications, including contact lenses, disinfectant hand gels, polymer optical fibers, monoliths for capillary electrochromatography, lithography, adhesives and coatings [15-17]. The use of benzyl methacrylate in medical materials gives the polymer important properties such as flexibility, transparency, and resistance. Polymers' mechanical and physical properties can also be improved by adding carbon-based fillers such as graphite to synthesized copolymers. Graphite is an inexpensive inorganic material that is abundant in nature and prepared synthetically. When added to the matrix phase, it has a significant effect on the electrical and thermal conductivity, barrier properties and mechanical properties of materials. It is frequently used to improve the electrical conductivity, antistatic properties and thermal conductivity of plastics [18-20]. Therefore, in this study, graphite was added to (benzyl methacrylate-co-styrene) copolymer to investigate the machinability temperature and thermal strength of the composite structure and to study the thermal degradation kinetics.

2. Experimental

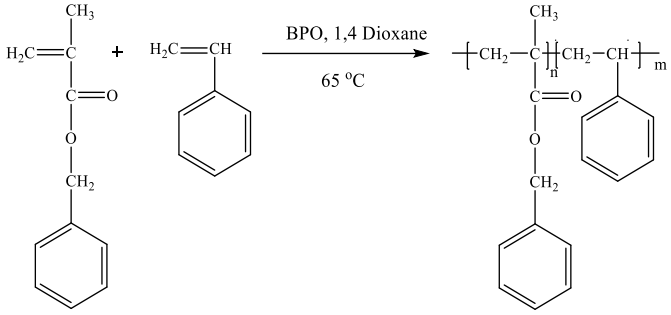
2.1. Materials and Instrumentation

Benzyl methacrylate and styrene purchased commercially from Sigma-Aldrich., were distilled under reduced pressure before copolymerization. 1,4-Dioxane and dichloromethane were used as received. In free radical polymerization, AIBN (2,2'-azobisisobutyronitrile), was used as initiator after crystallization. The graphite was obtained from Sigma Aldrich.

Fourier Transform Infrared (FT-IR) spectra of the studied polymer and composites were recorded in the range of 4000–400 cm-1 using a Perkin Elmer Spectrum 100. Proton nuclear magnetic resonance (1H-NMR; 400 MHz) spectra in the presence of $CDCl_3$ containing tetramethylsilane in the ppm level were measured by an AVANCE III 400 MHz Bruker NMR spectrometer. Thermal stabilities and glass transition temperatures of polymer and composites were conducted on a Seiko SII 7300 TG/DTA under nitrogen flow from 25°C to 500 °C at the heating rate of 20 °C/min.

2.2. Preparation of polymer and composites

Random copolymer P(BzMA0.33-co-St) was synthesized in a solvent at 65 °C, using AIBN as the initiator. The free radical polymerization method was employed to prepare the copolymer. Following an 18-hour polymerization period, the polymers were allowed to cool to ambient temperature, precipitated in excess ethyl alcohol, and then vacuum-dried for 24 hours at 40 °C. The chemical structure of the copolymer is illustrated in Scheme 1.



Scheme 1. *Synthesis of P(BzMA-co-St)*

The composites were produced in four steps using different proportions of graphite as a filler material (1, 5, and 10% by weight). First, 1%, 5%, and 10% graphite (by weight according to the amount of polymer) were taken into three separate beakers with dichloromethane solvent and dispersed in a Bandelin Ultrasonic Homogenizer Sonicator for about one hour. Second, P(BzMA0.33-co-St) copolymer was completely dissolved in 20 mL of dichloromethane and the polymer solution prepared in the third step was added to the graphite dispersed in dichloromethane. Finally, the resulting mixture was mechanically stirred for one hour to ensure homogeneous distribution and the solvent was removed in the evaporator. The composites produced were dried in a vacuum oven at 40 °C.

3. Results and Discussion

3.1. Characterization of Copolymer and Composites

Figure 1 displays FT-IR spectra of P(BzMA0.33-co-St) and its composites. The C-H stretching band of the aromatic ring was detected at 3092-3058 cm^{-1}. The methyl and methylene groups are represented by the symmetrical and asymmetrical stretching bands located at 2941 and 2884 cm^{-1} The ester carbonyl stretching vibration of the benzyl methacrylate is attributed to the band at 1720 cm^{-1}. The bands at 1167 cm^{-1} and 1257 cm^{-1} are symmetric and asymmetric stretching of the –C(=O)-O-C group. Moreover, mono-substituted benzene's aromatic C-H stretching vibration was detected at 691 cm^{-1}. The carbonyl peak and some peak shifts were observed when graphite was added to the polymer. The ^{1}H-

NMR spectrum of the P(BzMA0.33-co-St) copolymer, shown in Figure 2, reveals several key peaks that characterize the copolymer. The aromatic ring protons from the styrene and benzyl methacrylate units appear between 7.4 and 6.5 ppm. The OCH_2 protons in the benzyl methacrylate units are observed at 4.9 ppm. The CH_2 protons in the main chain are between 2.2 and 1.1 ppm, while the CH_3 protons in the polymer chain are at 1.1 to 0.5 ppm. These peaks provide essential information about the composition of the copolymer.

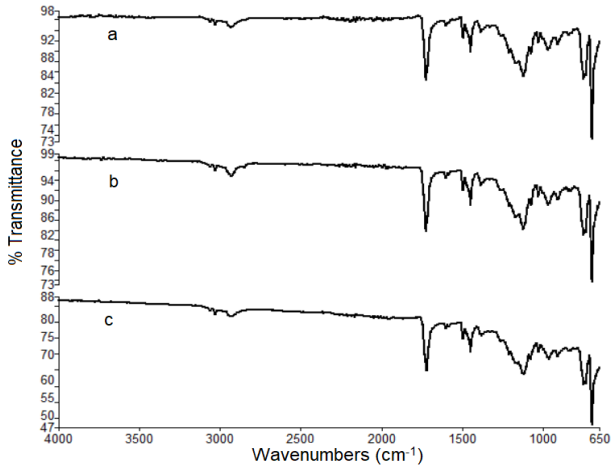


Fig. 1. FT-IR Spectrum of a-) P(BzMA0.33-co-St) b-) P(BzMA0.33-co-St)/G 5 wt% c-) P(BzMA0.33-co-St)/G 10 wt%

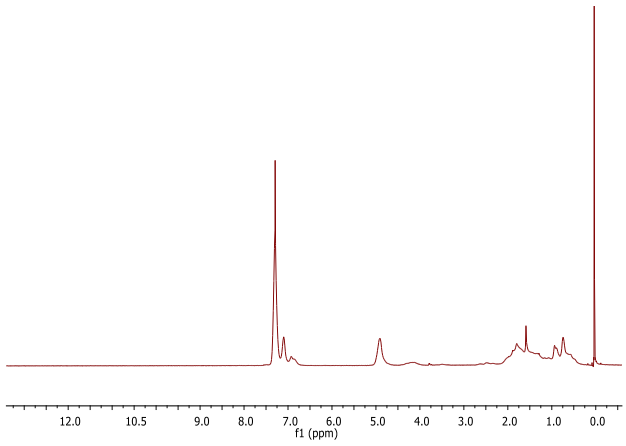


Fig. 2. ^{1}H-NMR Spectrum of P(BzMA0.33-co-St)

Using the ^{1}H-NMR spectra, the percentage compositions of P(BzMA-co-St) copolymers were determined. The aromatic ring protons from the styrene and benzyl methacrylate units between 7.4 and 6.5 ppm (integral height of aromatic protons=7.6) and the OCH_2 protons at 4.93 ppm in the BzMA units (integral height of OCH_2 protons=1) served as the foundation for determining the composition percentages. The following formulas were employed to determine these compositions.

$$\frac{\text{integral height of aromatic protons}}{\text{integrall height of OCH2 proton}} = \frac{5m1+5m2}{2m2} \quad (1)$$

m_1 represents the BzMA mole fraction and m_2 represents the St mole fraction. If $m_1+m_2=1$, then $m_2=1-m_1$ because the total mole fraction is always equals 1. The calculation method of the copolymer compositions for the P(BzMA0.33-co-St) polymer sample is as follows.

$$\frac{5m1+5m2}{2m2} = \frac{7.6}{1} \quad (2)$$

It is calculated as % m_1=0.33 and % m_2 =1-m_1=0.67.

3.2. Thermal behaviors

The glass transition temperatures of the studied polymers and composites were investigated by differential thermal analysis (DTA) from room temperature to 200 ºC under N_2 atmosphere at a heating rate of 20 ºC/min. This temperature is an important and characteristic value for polymer processing. The glass transition temperature of the polymer was determined by taking the midpoint of the sloping region on the DTA curve in Figure 3. While the glass transition temperature of P(St) and P(BzMA) in the literature is approximately 100 ºC and 54 ºC, it was determined as 88 ºC for P(BzMA 0.33-co-St) copolymer. The glass transition temperatures of the composites of the copolymer containing 1 wt%, 5 wt% and 10 wt% graphite were calculated as 80, 82 and 87 ºC, respectively and given in Table 1.

The thermal behavior of a polymer can be significantly changed by adding a fill to the polymer chain. Investigating the prepared materials' thermal behavior is therefore crucial. Thermal behaviors of studied polymer and composites were examined by thermogravimetric analysis (TGA) in the temperature range of 25−500 ºC at 20 ºC/min under N_2 atmosphere. When the TGA thermograms of the synthesized polymers were examined, it was found that the initial decomposition temperature for P(BzMA) was 212 °C and 373 °C for P(St). It was also observed that the initial decomposition temperatures and thermal stability of P(BzMA0.33-co-St) increased with increasing St content in the copolymer composition.

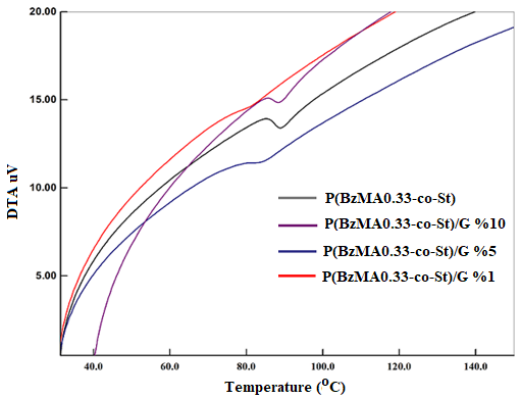


Fig. 3. DTA curves of P(BzMA0.33-co-St) and its composites

The thermo-gravimetric (TG) curves of composites and copolymer are contrasted in Figure 4. P(BzMA0.33-co-St)/G 10 wt% has demonstrated an initiation degradation temperature of 327 ^{o}C, whereas P(BzMA0.33-co-St) has presented an initiation degradation temperature of around 311 ^{o}C. The temperatures for P(BzMA0.33-co-St) and P(BzMA0.33-co-St)/G 10 wt% were found to be 383 and 380 ^{o}C, respectively, when the temperatures corresponding to 50% degradation by weight were used as a metric for the thermal stability of copolymers and composites. Furthermore, waste rose proportionately to the polymer chain's graphite content. Table 1 compares the degradation properties of the polymer and its composites.

Table 1. TGA values of P(BzMA-co-St) and its composites

Polymer	T_g (^{o}C)	$T_{baş}$ (^{o}C)	$T_{\%10}$ (^{o}C)	$T_{\%50}$	$T_{\%90}$	Residue
P(BzMA0.33-co-St)	88	311	348	383	406	0.18
P(BzMA0.33-co-St)/G 1%	80	316	338	376	405	1.27
P(BzMA0.33-co-St)/G 5%	82	327	346	381	414	4.67
P(BzMA0.33-co-St)/G 10%	87	327	345	380	414	7.42

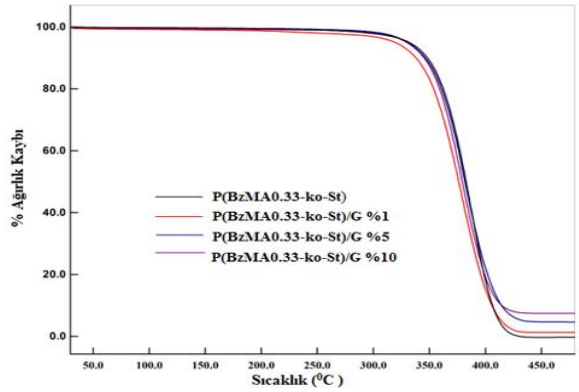


Fig. 4. TGA curves of P(BzMA0.33-co-St) and its composites

3.3 Thermal Degradation Kinetics

Kinetic parameters are determined using isoconversion methods to gain insight into the thermal degradation processes of polymers. Although these methods can be time-consuming, they are highly effective for accurately obtaining the activation energy associated with thermal degradation. Two commonly used "model-free" approaches, the Kissinger-Akahira-Sunose (KAS) [21]. and the Flynn-Wall-Ozawa (FWO) [22-23]. methods, allow for the estimation of activation energy (Ea) based on the degree of conversion (α). Ea is a crucial and practical kinetic parameter in thermal decomposition processes. These techniques help avoid errors that may arise from the choice of a reaction mechanism, as they do not rely on any specific reaction model when calculating activation energy. Thermogravimetry (TG), differential thermogravimetry (DTG), or differential scanning calorimetry (DSC) can be employed for kinetic research. The thermogravimetric method analyzes mass loss curves obtained at various heating rates to assess the impact of kinetic parameters on conversion. Conversion values are derived from TG data at each temperature increment. This study investigated the thermal degradation processes of the P(BzMA0.33-co-st) copolymer and its composite containing 10 wt% graphite using the FWO and KAS methods.

The Flynn-Wall-Ozawa (FWO) analysis method is crucial in kinetic studies. This method allows for the determination of kinetic properties solely from experimental data. The activation energy (Ea) is calculated by plotting 1/T against log(β) for a specific conversion value (α) across various heating rates (β). The resulting graph of 1/T versus log(β) should yield a straight line. The activation energy can be determined from the slope of this line using the appropriate formula.

$$\log(\beta)=\log [AEa/g(a)R]-2.315-(0.457\ Ea)/RT \quad (3)$$

In equation 3; β is the heating rate (°C min $^{-1}$), R is the gas constant (8.314 J/mol), α is the extent of conversion and Ea is the activation energy.

In this study, the activation energies of the copolymer and its composites were investigated using TG analysis curves. As seen in Figure 5, TGA curves of P(BzMA0.33-co-St) were obtained from 30 to 500 ^{o}C, under a nitrogen flow (20 mL min^{-1}) at 5, 10, 15, and 20 ^{o}C/ min heating rates. The average activation energy value for P(BzMA0.33-co-St) copolymer at different conversions (α = 0.1-0.9) was determined using the slope lines of the log B versus 1000/T (K-1) plot as shown in Figure 6. The activation energy is estimated by Eq. (3) according to the FWO method. These results calculated the polymer's average activation energy value as 148.898 kJ/mol for conversions between 0.1 and 0.9.

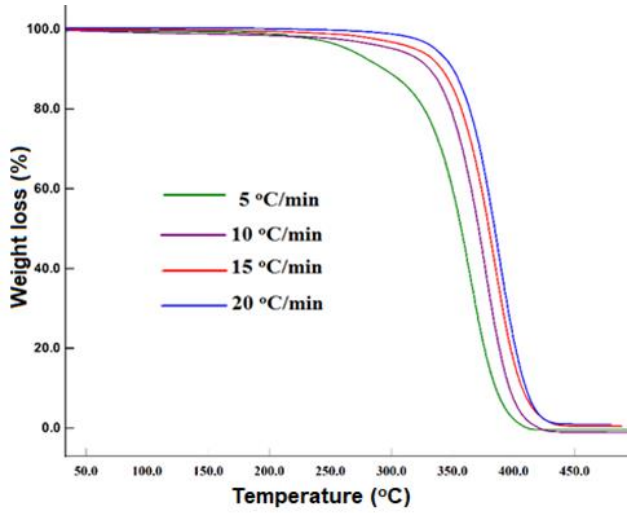


Fig. 5. TGA curves of poly(BzMA0.33-co-St) at different heating rate

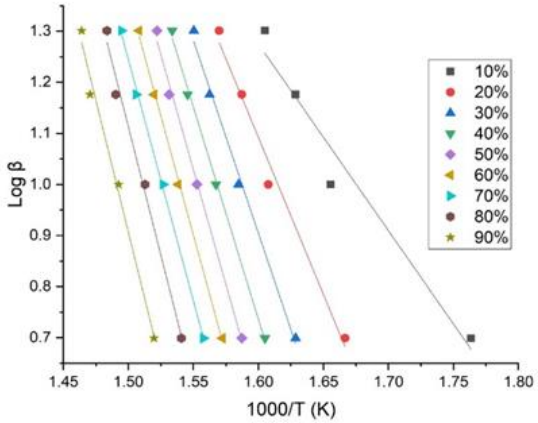


Fig. 6. Isoconversional plot of FWO method for poly(BzMA0.33-co-St) for conversion of 0.1-0.9

On the other hand, the Kissinger-Akahira-Sunose (KAS) method was used to estimate the E_a values of P(BzMA0.33-co-St) in thermal degradation. The KAS method, one of the thermal analysis methods is one of the very important methods of estimating the activation energy, which is studied with the thermogravimetry (TG) technique. The KAS equation can be defined as the following (4):

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{g(\alpha)Ea}\right) - \frac{Ea}{RT} \quad (4)$$

According to Eq. (4), the activation energy E_a can be calculated from a plot of $\ln(\beta/T^2)$ versus 1000/T (K^{-1}) for a constant value of α where the slope equals $-E_a/R$. As seen in Figure 7, plotting $\ln(\beta/T^2)$ against 1000/T (K^{-1}) produces a straight line.

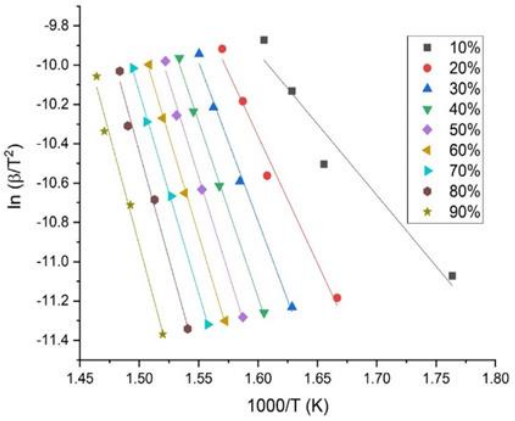


Fig. 7. Isoconversional plot of KAS method for poly(BzMA0.33-co-St) for conversion of 0.1-0.9

The E_a values estimated for different heating rates such as 5, 10, 15, and 20 °C/min are shown in Table 2. According to these results, the polymer's average activation energy value was calculated as 146,431 kJ/mol for conversions in the range of 0.1 to 0.9.

Table 2. TGA values of P(BzMA-co-St) and its composites

Flynn–Wall–Ozawa (FWO) method		Kissinger-Akahira-Sunose (KAS) Method	
Conversion/α	**Ea (kJ/mol)**	**Conversion/α**	**Ea (kJ/mol)**
0.1	66,524	0.1	60,165
0.2	111,930	0.2	107,542
0.3	137,407	0.3	134,154
0.4	151,192	0.4	148,529
0.5	163,662	0.5	161,549
0.6	169,551	0.6	167,651
0.7	171,913	0.7	170,037
0.8	182,955	0.8	181,561
0.9	187,955	0.9	186,690
Average	148,898	**Average**	146,431

As shown in Figure 8, thermogravimetric analysis of P(BzMA0.33-co-St)/ G 10 wt% composite was performed at four different heating rates. With the help of the data obtained from the analysis, activation energy values were calculated from Eq. (3) for the FWO method and Eq. (4) for the KAS method. The lines obtained according to the FWO method are shown in Figure 9 and the lines obtained by the KAS method are shown in Figure 10.

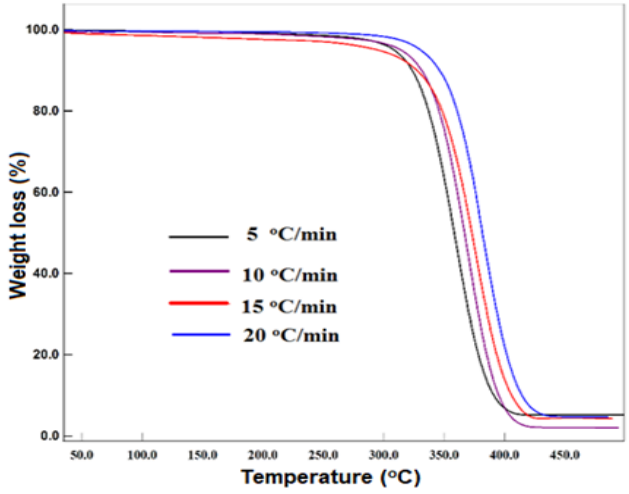


Fig. 8. TGA curves of poly(BzMA0.33-co-St)/G 10 wt%

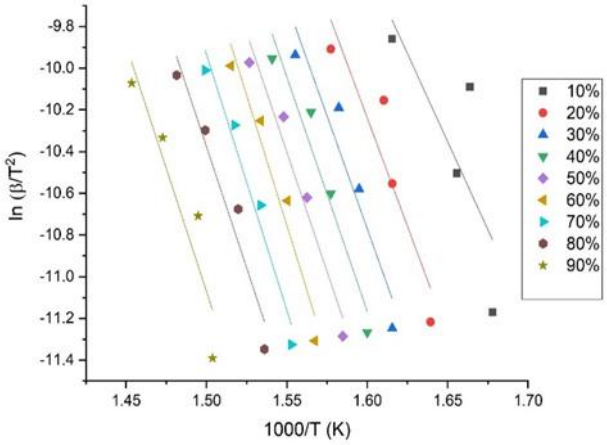


Fig. 9. Isoconversional plot of FWO method for poly(BzMA0.33-co-St)/G 10 wt% for conversion of 0.1-0.9

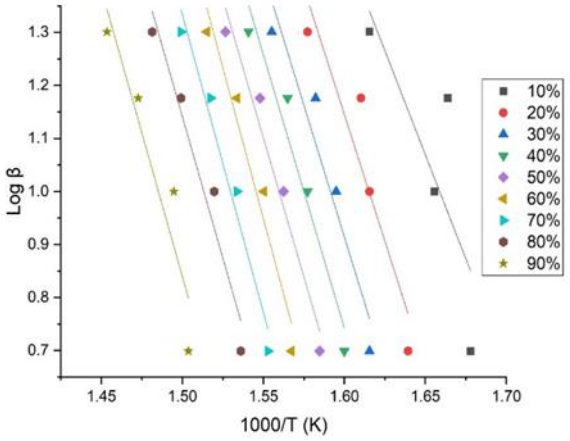


Fig. 10. Isoconversional plot of KAS method for poly(BzMA0.33-co-St)/G 10 wt% for conversion of 0.1-0.9

The apparent activation energies calculated at various conversions of poly(BzMA0.33-co-St)/G 10 wt% composite using FWO and KAS method are given in Table 3.

Table 3. Values of E_a for each conversion for FWO and KAS method for composit

Flynn–Wall–Ozawa (FWO) method		Kissinger-Akahira-Sunose (KAS) Method	
Conversion/α	**Ea (kJ/mol)**	**Conversion/α**	**Ea (kJ/mol)**
0.1	142,990	0.1	140,356
0.2	173,710	0.2	172,623
0.3	180,808	0.3	179,923
0.4	187,538	0.4	186,774
0.5	190,904	0.5	190,230
0.6	207,093	0.6	207,168
0.7	204,273	0.7	204,083
0.8	194,305	0.8	193,475
0.9	197,288	0.9	196,384
Average	186,545	**Average**	185,668

4. Conclusion

P(BzMA0.33-co-St) copolymer was synthesized by free radical polymerization at 65 °C. Composites were prepared with graphite added to the synthesized copolymer in three ratios (1%, 5% and 10% by weight). While the glass transition temperature of the pure copolymer was 88 C, the glass transition temperature of the composite containing 1 wt%, 5 wt%, and 10 wt% graphite by weight was found to be 80, 82, and 87 °C, respectively. The glass transition temperatures of the composites were calculated to be lower than the pure copolymer. The effect of the added filler on the thermal stability of the copolymer was determined from the TGA curves. The initial decomposition temperature of the pure copolymer was defined as 311 °C from TGA measurements, while that of the composites increased from 316 °C to 327 °C. Pure copolymer and P(BzMA-co-St)/G 10 wt% activation energies were measured from TGA measurements at different heating rates. In this context, the average activation energy values estimated by both FWO and KAS methods were 148,898 kJ/mol and 146,431 kJ/mol for the copolymer and 186,545 kJ/mol and 185,668 kJ/mol for the composite, respectively. The lower glass transition temperature of the studied copolymers and composites compared to styrene will provide ease of processing and shaping of these materials and ease of design for manufacturers in industrial applications.

Acknowledgments

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