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THE SYNTHESIS OF ALLYL GLYCIDYL ETHER COPOLYMERS AND THEIR THERMOKINETIC ANALYSIS

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ABSTRACT

The copolymerization reactions of allyl glycidyl ether (AGE) by radicalic polymerization under argon atmosphere using benzoyl peroxide (BPO) as an initiator with the comonomers of allyl methacrylate (AMA) and methyl methacrylate (MMA) were studied. The synthesized copolymers were characterized by nuclear magnetic resonance (^{1}H-NMR), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TG). FTIR and ^{1}H NMR spectra showed that the pendant epoxy groups in copolymers remained throughout the copolymerization of AGE. The apparent activation energies for thermal degradation of the copolymers were calculated from their TG data by using Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Coats-Redfern methods. The kinetic parameter (pre-exponential factor) and Thermodynamic parameters such as Gibbs energy, enthalpy and entropy were also calculated by Coats-Redfern method. The activation energies calculated by KAS method for Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) were found to be 292±10 kJ/mol and 175±27 kJ/mol for the first stage, and 252±74 kJ/mol and 232±32 kJ/mol for the second, respectively while they were 361±1 kJ/mol and 249±61 kJ/mol for Poly(AGE-*co*-AMA) and 136±24 kJ/mol and 278±18 kJ/mol for Poly(AGE-*co*-MMA) by FWO method.

The most likely mechanisms of the main degradation stages were determined as F_3 model for Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA). Thus, it is concluded that the thermal degradations of Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) copolymers exhibit similar behavior.

Keywords: Thermal degradation, Allyl glycidyl ether, Allyl methacrylate, Methyl methacrylate

1. INTRODUCTION

Epoxy resins combine good thermal and dimensional stability, excellent chemical and corrosion resistance, high tensile strength and modulus, and ease of handling and processability, ensuring their wide applications to industrial fields such as coatings, adhesives and insulating materials [1-4]. Many attempts have been made in developing advanced technologies in order to improve the thermal properties of the high-performance epoxy resins [2]. Allyl glycidyl ether has a conjugated epoxy group and an unconjugated allylic group. Because of their higher reactivities, bifunctional monomers containing two reactive groups can be used for the preparation of functional (co)polymers. The thermal degradation behaviors of the epoxy containing homo- and copolymers have been discussed previously [5-8]. Investigating the degradation of the polymers is of importance in understanding their processing, application, and thermal recycling. The common methods of polymer degradation are bio-, photo-oxidative, ozone-induced, mechanochemical, thermal and catalytic degradations [9-13].

In the present study, the thermal degradation kinetics of the epoxy containing Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) copolymers synthesized by radicalic polymerization were investigated to compare their thermal properties since the thermal properties of which are very important from the viewpoint of their usages. For this purpose, the apparent activation energies for thermal degradation of the copolymers were determined by using FWO, KAS and Coats-Redfern methods. Also the kinetic and thermodynamic parameters (pre-exponential factor, Gibbs energy, enthalpy, and entropy) and the degradation mechanism of the copolymers were also studied by Coats-Redfern method.

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1.1. Kinetic Analysis [14-16]

Thermogravimetric analysis can be used for determining the degradation kinetics of a lot of polymers. In general, the thermal degradation reaction of a solid polymer can be shown as:

$$A_{solid} \rightarrow B_{solid} + C_{gas}$$

where A is the starting material, B_{solid} and C_{gas} are the solid residue and the gas product, respectively.

The thermal degradation kinetics of the polymers is generally expressed by the following typical kinetic equation

$$r = \frac{d\alpha}{dt} = k(T) \times f(\alpha) \tag{1}$$

where T is the absolute temperature (K); r is the conversion per unit time (t) and f(α) is the conversion function which represents the reaction model. The degree of conversion (α) is calculated by Eq. (2) where m_o, m_t and m_f are the weights of sample before degradation, at time t and after complete degradation, respectively.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{2}$$

k is the reaction constant which can be expressed by the Arrhenius equation:

$$k(T) = A_0\, e^{-\left(\frac{E_a}{RT}\right)} \tag{3}$$

where A is called pre-exponential factor, E_a is the activation energy and R is the gas constant.
By combining Eq. (1) and Eq. (3) the following equation is obtained

$$\frac{d\alpha}{dt} = A_0\, e^{-\left(\frac{E_a}{RT}\right)} \times f(\alpha) \tag{4}$$

According to the kinetic theory for the non-isothermal decomposition reactions, the fractional conversion α is expressed as a function of temperature which depends on the time of heating. Thus the heating rate (β) can be described as:

$$\beta = \frac{dT}{dt} \tag{5}$$

that Eq. (4) is modified as follows:

$$\frac{d\alpha}{dT} = \left(\frac{1}{\beta}\right) A_0\, e^{-\left(\frac{E_a}{RT}\right)} \times f(\propto) \tag{6}$$

Eq. (4) and Eq. (6) are the basis for the many equations derived to evaluate thermal analysis data.

1.1.1. Flynn-Wall-Ozawa (FWO) method [17,18]

The activation energy can be determined by this method with no need of any knowledge for the reaction mechanism. The pre-exponential factor (A) and the activation energy (E_a) are not dependent on the fraction of degradation while they are on the temperature. This method uses Eq. (7).

$$\boldsymbol{log\ g(\alpha) = log\ \left(\frac{AE_a}{R}\right) - log\beta + log\ p\ \left(\frac{E_a}{RT}\right)} \qquad (7)$$

Eq. (8) is obtained by means of the Doyle approximation.

$$\boldsymbol{log\ \beta\ = log\ \left(\frac{AE_a}{R}\right) - log\ g(\alpha) - 2{,}315 - 0{,}4567\ \left(\frac{E_a}{RT}\right)} \qquad (8)$$

Hence, from the slope -E_a/R of the linear plot of log β versus 1000/T, E_a is readily obtained.

1.1.2. Kissinger-Akahira-Sunose (KAS) method [19,20]

The KAS method is based on the following equation

$$\boldsymbol{ln\ \left(\frac{\beta}{T^2}\right) = ln\ \frac{AR}{E_a\, g(\alpha)} - \left(\frac{E_a}{RT}\right)} \qquad (9)$$

where the plots of ln(β/T^2) versus 1000/T for the several α values give straight lines with the slope of –E_a/R which give the corresponding E_a values.

1.1.3. Coats-Redfern method [21]

This method is based on the following equation

$$\boldsymbol{ln\ \left(\frac{g(\alpha)}{T^2}\right) = ln\ \left(\frac{AR}{E_a\beta}\left(\frac{1-2RT}{E_a}\right)\right) - \left(\frac{E_a}{RT}\right)} \qquad (10)$$

as E_a is calculated from the slope –E_a/R of the plot ln (g(α)/T^2) versus 1000/T which is a straight line. The possible thermal degradation mechanism can also be estimated from the most commonly used reaction models for the solid-state processes listed in Table 1[16].

Table 1 Algebraic expressions of f(α) and g(α) for the reaction models [16] considered in the present work

Symbol	Reaction model	f(α)	g(α)
Sigmoidal curves			
A₂	Avrami–Erofĕev (n = 2) (Nucleation and growth)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A₃	Avrami–Erofĕev (n = 3) (Nucleation and growth)	$3(1-\alpha)[-\ln(1-\alpha)]^{-1/2}$	$[-\ln(1-\alpha)]^{1/3}$
A₄	Avrami–Erofĕev (n = 4) (Nucleation and growth)	$4(1-\alpha)[-\ln(1-\alpha)]^{-1/3}$	$[-\ln(1-\alpha)]^{1/4}$
Deceleration curves			
R₁	Zero-order (Polany–Winger equation) Phase-boundary controlled reaction (one dimensional movement)	1	α
R₂	Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$2(1-\alpha)^{1/2}$	$[1-\ln(1-\alpha)^{1/2}]$
R₃	Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$3(1-\alpha)^{2/3}$	$[1-\ln(1-\alpha)^{1/3}]$
F₁	First-order (Mampel) (Random nucleation with two nuclei on the	(1−α)	ln(1−α)

	individual particle)		
***F*₂**	Second-order (Random nucleation with two nuclei on the individual particle)	$(1-\alpha)^2$	$1/(1-\alpha)$
***F*₃**	Third-order (Random nucleation with two nuclei on the individual particle)	$1/2(1-\alpha)^3$	$1/(1-\alpha)^2$
***D*₁**	One-dimensional diffusion	$1/2\alpha$	α^2
***D*₂**	Two-dimensional diffusion (bidimensional particle shape) Valensi equation	$-1/[\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha) + \alpha$
***D*₃**	Three-dimensional diffusion (tridimensional particle shape) Jander equation	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{-1/3}]$	$[1-\ln(1-\alpha)^{1/3}]^2$
***D*₄**	Three-dimensional diffusion (tridimensional particle shape) Ginstling–Brounshtein	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

2. EXPERIMENTAL

2.1. MATERIALS

Allyl glycidyl ether (AGE), methyl methacrylate (MMA) and allyl methacrylate (AMA) with the purities of 97, 99 and 98 percent, respectively, as it is with all other chemicals, purchased from Merck A.G (Germany). They were used without any further purification.

2.2. Copolymerization

10 mmol of AGE and comonomer (MMA or AMA) and 0.1 mmol of benzoyl peroxide (BPO) were placed into a pyrex flask. The polymerization was carried out at 70°C for 2 hours under argon atmosphere. The solid copolymers were precipitated pouring the polymer solution into methanol.

2.3. Characterization of the Copolymers

FTIR spectra of the copolymers were taken on Perkin Elmer Spectrum 100 FT-IR Spectrometer (USA) using KBr pellets. ^{1}H-NMR spectra of the copolymers were taken in $CDCl_3$ as solvent by means of a Varian 400MHz NMR Spectrometer (USA). Molecular weights were determined by gel permeation chromatography (GPC) instrument equipped with a Waters (USA) styragel column (HR series 2, 3, 5E) with tetrahydrofuran as the eluent at a flow rate of 0.3 mL/min and a Waters 410 differential refractometer detector. The TG curves were recorded by using a Perkin Elmer, Diamond TG/DTA(USA). The samples were heated under argon atmosphere over a temperature range 30 to 600°C with heating rates of 5, 10, 15, 20°C/min. The weight loss (TG curve) and its first derivative (DTG curve) vs. temperature were recorded simultaneously. The solid sample weights for all the experiments were taken in the range of 8-10 mg.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Copolymers

Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) were synthesized by copolymerization of AGE with AMA and MMA as comonomers in bulk at 70°C, in the presence of BPO as initiator. It was proved by FTIR (Figure 1) and ^{1}H-NMR (Figure 2) spectroscopy that the polymerization has occurred. As seen in Fig 1, the FTIR absorption bands for C=O bond of the Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) copolymers take place around 1700 cm^{-1} while the characteristic strong absorption band of the ether group appears at 1100 cm^{-1}, and two bands for C-H bending appear at 1233 and 855 cm^{-1}. As far as ^{1}H-NMR spectra are concerned Poly(AGE-*co*-MMA) exhibits characteristic peaks for CH_3 protons between 0.5 and 1.0 ppm. Additionally, CH_3-O protons were detectable as a sharp signal at 3.7 ppm. ^{1}H-NMR spectrum of Poly(AGE-*co*-AMA) was not achieved because a suitable solvent was not found to solve it.

M_n (number-average molecular weight) and the polydispersity index (PDI) of the Poly(AGE-co-MMA) was measured by GPC as the results are 65000 g/mol for M_n, and 2.30 for PDI, respectively. The molecular weight of Poly(AGE-*co*-AMA) copolymer was not achieved because a suitable solvent was not found to solve it. Molecular weight of Poly(AGE-*co*-AMA) was not determined because of solubility problem.

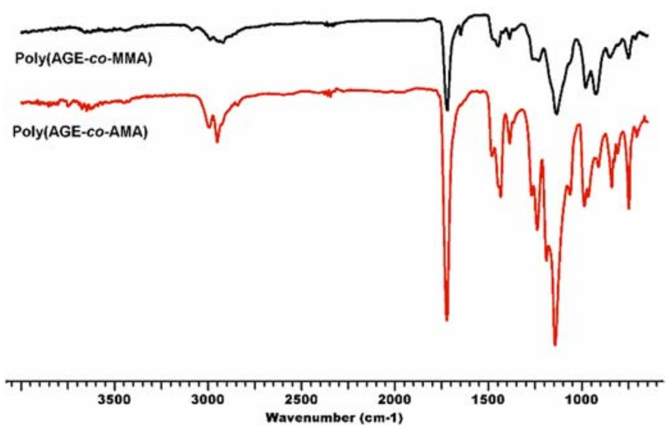

Figure 1. FTIR spectra of Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA)

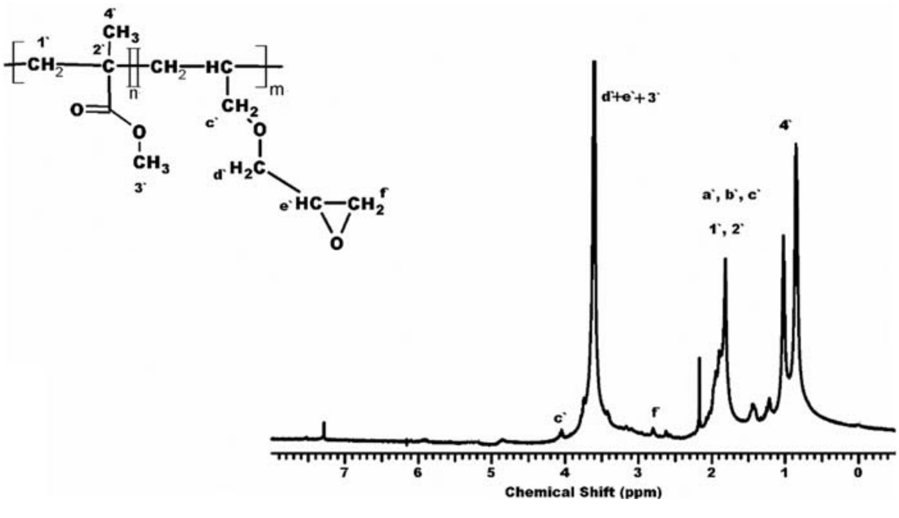

Figure 2. ^{1}HNMR spectrum of Poly(AGE-*co*-MMA)

3.2. Thermogravimetric Analysis of the Copolymers

Fig. 3 and 4 show the respective TG and DTG thermograms of Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) under argon atmosphere over a temperature range 30 to 600ºC with a heating rate of 10ºC/min. The initial (T_i), maximum (T_{max}) and final (T_f) degradation temperatures related to the thermograms are summarized in Table 2.

Table 2. Initial (T_i), maximum (T_{max}), and final (T_f) degradation temperatures for the thermal degradation of the copolymers

Copolymer	**T_i(°C)**		**T_{max} (°C)**		**T_f (°C)**	
	First stage	**Main stage**	**First stage**	**Main stage**	**First stage**	**Main stage**
Poly(AGE-*co*-AMA)	250	350	305	420	350	497
Poly(AGE-*co*-MMA)	175	253	172	382	240	452

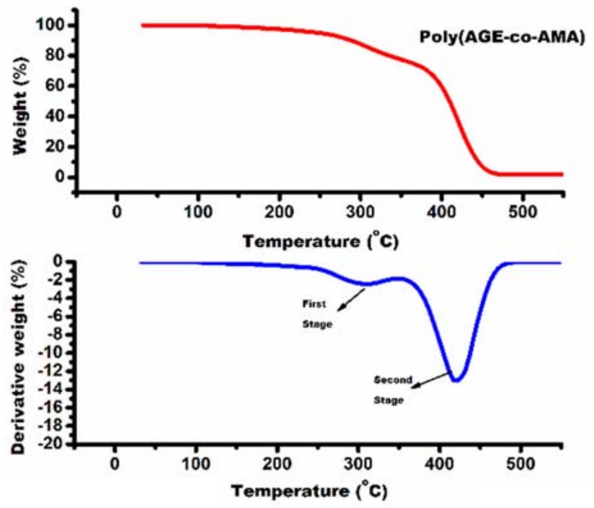

Figure 3. The TG and DTG thermograms of Poly(AGE-*co*-AMA) in argon atmosphere at 10 °C/min

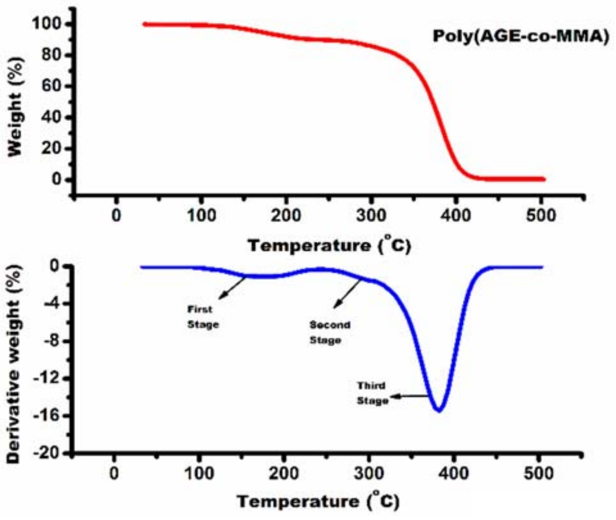

Figure 4. The TG and DTG thermograms of Poly(AGE-*co*-MMA) in argon atmosphere at 10 °C/min

The thermogram of Poly(AGE-*co*-AMA) exhibited the copolymer has degraded in two stages. The T_{max} was about 420°C while the half-life temperature ($T_{1/2}$) was about 409°C. The similar thermal degradation behavior has been reported for Poly(allyl methacrylate) (PAMA) by Vardarel, et. al. and Zulfiqar et. al. [22, 23] as T_{max} and $T_{1/2}$ being around 409°C and 400°C, respectively. Solpan et al. has reported T_{max} and $T_{1/2}$ for Poly(allyl glycidyl ether) (PAGE) homopolymer to be 443°C and 434°C, respectively [24]. A residue of about 5.0 % remained over 600^{o}C for PAGE, while PAMA and Poly(AGE-*co*-AMA) degraded completely at this temperature. Thus, the degradation temperatures of the AGE copolymer with AMA seems to decrease average 25^{o}C compared to that of PAGE homopolymer indicating that the copolymer is less stable than the homopolymer. However the degradation temperatures of the copolymer are quite similar to those of PAMA homopolymer i.e. both having the same stability. According to the TG data, various products such as CO, CO_2, -CN, $-CH_2-CH=CH_2$, $-O-CH_2-CH=CH_2$, $-C(=O)-O-CH_2-CH=CH_2$, anhydride structures and also the monomer are obtained in the two stage degradation of PAMA [22]. The first degradation stage of Poly(AGE-*co*-AMA) in the range of 250 to 350^{o}C may be due to the destruction of carbonyl units and methacrylate groups which are more sensitive to degradation while the second degradation stage in the range of 350 to 497^{o}C is possibly because of the degradation of polymer chain itself.

As far as thermal degradation of Poly(AGE-*co*-MMA) is concerned, two degradation stages are observed again with the weight losses of 6 % and 94 % for first and second (main) stages, respectively. The thermal degradation of the radiation induce synthesized Poly(AGE-*co*-MMA) has also been reported to occur in two stages as described earlier [24]. The T_{max} of the second stage for Poly(AGE-*co*-MMA) and $T_{1/2}$ were found to be 403^{o}C and 390^{o}C, respectively. In the present work T_{max} and $T_{1/2}$ were found to be 383^{o}C and 372^{o}C. The differences in the values may arise due to the different copolymerization methods.

Very weak peak with T_{max} = 175°C is observed in the DTG curves of Poly(AGE-*co*-MMA) over the temperature range 100 to 230°C with the weight losses of 3%. It was reported that the PMMA obtained by radicalic polymerization may contain some head to head linkages and some early degradation which occur around 140-150^{o}C is due to the cease of these linkages because the bond dissociation energy of such bonds is low in comparison to that of the C-C bonds mainly due to steric and inductive effects of vicinal ester groups. The second degradation stage which occurs around 230-255^{o}C seems due to the unsaturated chain ends resulting from the termination by disproportionation [25, 26]. The degradation stage in present work is a very weak peak with T_{max} around 255^{o}C. The thermal degradation in both the first and second stage leading to a weight loss of nearly 5-6% ends before approximately 360^{o}C where the third and main stage of degrading process involving random scission starts.

In order to obtain detailed information related to the thermal stability of the copolymers the kinetic and thermodynamic parameters such as activation energy, pre-exponential factor, Gibbs energy, enthalpy and entropy of the degradation were calculated using FWO, KAS and Coats-Redfern methods. Also the degradation kinetics of the main degradation stage was investigated to determine the degradation mechanism. First FWO and KAS methods were used to analyze the TG data of Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) because they were independent of any thermal degradation mechanism. Then the results obtained were compared with that of Coats-Redfern method to conclude the true mechanism and to find out the rest of the kinetic and thermodynamic parameters.

3.3. Thermal Degradation Kinetics of the Copolymers

Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) were heated thermogravimetrically under various heating rates such as 5, 10, 15, and 20^{o}C/min in a temperature range of 30 to 600^{o}C to determine their thermal degradation mechanisms and the activation energies. The TG curves obtained for the copolymers are shown in Fig. 5 and 6, respectively. The individual degradation behavior of each copolymer was analogous at all heating rates as seen from the figure. The apparent activation energies and thermal degradation models for the copolymers were estimated by FWO, KAS and Coats-Redfern.

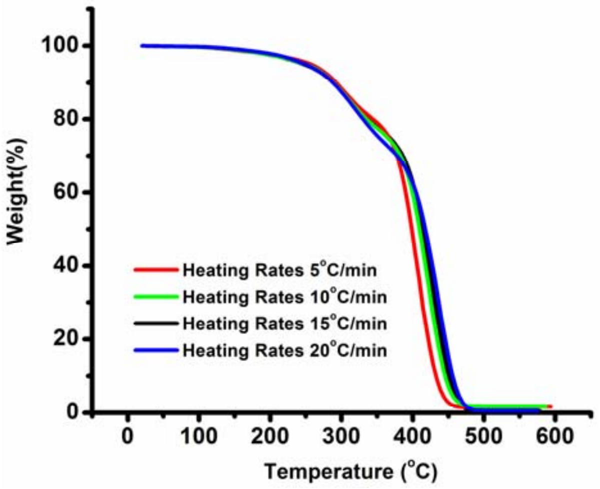

Figure 5. The TG thermograms of Poly(AGE-*co*-AMA) in argon atmosphere at different heating rates (5, 10, 15, 20 ºC/min)

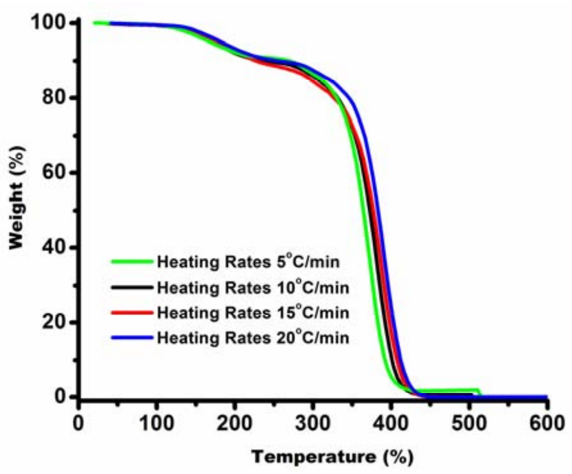

Figure 6. The TG thermograms of Poly(AGE-*co*-MMA) in argon atmosphere at different heating rates (5, 10, 15, 20 ºC/min)

The activation energies for Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) were found to be 361±1 and 136±24 for the first, and 249±61 and 278±18 for the second (main) stage, respectively by means of the classical FWO method. The average activation energies were calculated by KAS method for Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) as 292±10 and 175±27 for the first, and 252±74 and 232±32 for the second (main) stages, respectively. The calculated activation energies for Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) seem to be pretty higher than that of PAGE which is 72kJ/mol[24].

The plot of E_a vs. the degree of conversion is commonly used to indicate the degradation mechanism, i.e., it is one-step or more. As shown in Fig. 7, the mechanism changes throughout the degradation since E_a for Poly(AGE-*co*-AMA) exhibits varying values between 360 and 180 kJ/mol which means that Poly(AGE-*co*-AMA) has a complex degradation mechanism. The variation of the activation energies for the copolymer as a function of the degree of conversion (Fig. 8) showed that E_a increased up to 40% for Poly(AGE-*co*-MMA) then remained practically constant. The increase in the E_a values as a function of α is attributed essentially to thermally more stable structures because of the crosslinking reactions occurred during the progress of the thermal degradation [27].

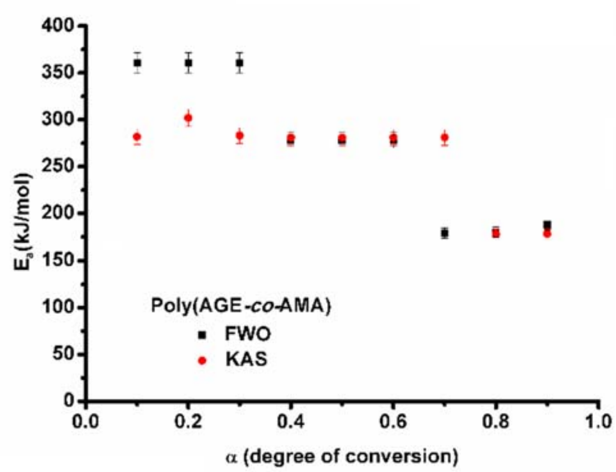

Figure 7. The plot of activation energy (E_a) vs. the degree of conversion (α) for Poly(AGE-*co*-AMA)

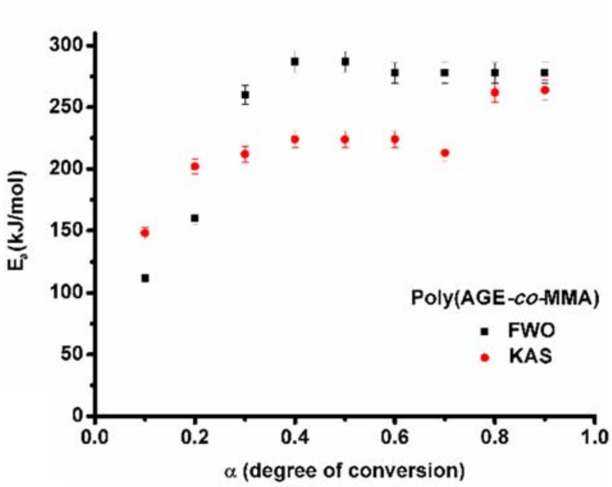

Figure 8. The plot of activation energy (E_a) vs. the degree of conversion (α) for Poly(AGE-*co*-MMA)

The thermal degradation mechanism of the copolymers for the main degradation stage is confirmed by comparing the mean activation energy value, $E_{a(FWO)}$, with those calculated by the Coats-Redfern method for different models in Table 1. The activation energies and correlations obtained from Coats-Redfern method at different heating rates are represented in Table 3 and 4. The E_a calculated from the $\boldsymbol{F}_3$ model is nearly the same with $E_{a(FWO)}$ for Poly(AGE-*co*-AMA) being 249 kJ/mol which leads to a conclusion that the most probable mechanism for the thermal degradation of Poly(AGE-*co*-AMA) is the third-order, $\boldsymbol{F}_3$ (random nucleation with two nuclei on the individual particle) for the heating rate of 15 °C/min.

Thermal degradation kinetics of Poly(AGE-*co*-MMA) copolymer shows that the activation energy obtained by FWO method is in good agreement with that of $\boldsymbol{F}_3$ model for the heating rate of 15°C/min. Consequently, the solid-state degradation mechanism of Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) have the same mechanism (integral form $1/(1-\alpha)^2$ for F_3).

Table 3. The degradation activation energies of Poly(AGE-*co*-AMA) calculated by Coats-Redfern method for different heating rates (5, 10, 15, 20 °C/min)

β (°C/min)	5		10		15		20	
Symbol	**Main stage Ea(kJ/mol)**	R^2	**Main stage Ea(kJ/mol)**	R^2	**Main stage Ea(kJ/mol)**	R^2	**Main stage Ea(kJ/mol)**	R^2
A_2	121	0.992	110	0.992	104	0.972	98	0.969
A_3	121	0.992	110	0.992	104	0.972	98	0.969
A_4	121	0.992	110	0.992	104	0.972	98	0.969
R_1	63	0.964	57	0.974	54	0.988	51	0.980
R_2	40	0.992	38	0.994	37	0.996	36	0.996
R_3	32	0.993	31	0.995	31	0.997	29	0.997
D_1	137	0.970	125	0.978	120	0.990	113	0.984
D_2	166	0.984	152	0.987	145	0.993	137	0.989
D_3	53	0.983	50	0.992	48	0.996	47	0.995
D_4	47	0.963	44	0.950	42	0.941	41	0.947
F_1	121	0.992	110	0.982	104	0.972	98	0.969
F_2	140	0.874	125	0.836	116	0.794	110	0.791
F_3	292	0.883	261	0.847	**244**	0.809	231	0.807

Table 4. The degradation activation energies of Poly(AGE-*co*-MMA) calculated by Coats-Redfern method for different heating rates (5, 10, 15, 20 °C/min)

β (°C/min)	5		10		15		20	
Symbol	**Main stage Ea(kJ/mol)**	R^2	**Main stage Ea(kJ/mol)**	R^2	**Main stage Ea(kJ/mol)**	R^2	**Main stage Ea(kJ/mol)**	R^2
A_2	127	0.997	126	0.991	126	0.988	136	0.988
A_3	127	0.997	126	0.991	126	0.988	136	0.988
A_4	127	0.997	126	0.991	126	0.988	136	0.988
R_1	66	0.945	66	0.974	66	0.981	71	0.940
R_2	41	0.988	38	0.985	41	0.996	43	0.983
R_3	32	0.989	33	0.995	33	0.997	34	0.985
D_1	142	0.953	144	0.978	144	0.984	152	0.949
D_2	172	0.973	174	0.989	173	0.993	185	0.967
D_3	54	0.983	54	0.993	54	0.995	57	0.978
D_4	48	0.977	48	0.959	47	0.953	51	0.966
F_1	127	0.997	126	0.991	126	0.988	136	0.988
F_2	149	0.909	144	0.836	143	0.843	159	0.899
F_3	308	0.914	300	0.865	**297**	0.852	329	0.905

3.4. Determination of Pre-Exponential Factor

The pre-exponential factor (A) was calculated by Coats-Redfern method from the solid-state degradation for each of the mechanisms obtained for the copolymers as shown in Table 5 and 6.

In the Coats-Redfern method told about, lnA is calculated from the intersection of the y axis (when x=0 y=lnAR/βE$_a$ neglecting (1-2RT/E)) using Equation 10 [28].

3.5. Determination of Enthalpy, Entropy and Gibbs Energy of Activation

The thermal degradation parameters i.e. activation enthalpy ($\Delta H^{\neq}$), entropy ($\Delta S^{\neq}$) and Gibbs energy ($\Delta G^{\neq}$) are calculated using Equations 11, 12, and 13, respectively [29].

$$E_a = \Delta H^{\neq} - RT_{max} \quad (11)$$

$$\boldsymbol{A} = \frac{\boldsymbol{k\,T_{max}}}{\boldsymbol{h}}\, e^{\Delta S^{\neq}-RT_{max}} \qquad (12)$$

$$\boldsymbol{\Delta G^{\neq} = \Delta H^{\neq} - T_{max}\Delta S^{\neq}} \qquad (13)$$

where k is Boltzmann constant, h is Planck constant and T_{max} is the temperature related to DTG peak maximum. All kinetic and thermodynamic parameters of the thermal degradation calculated from the thermogravimetric curves for the conversions in main degradation stage are listed in Table 5 and 6.

The activation enthalpy is positive because the degradation is an endothermic process for both of the copolymers. The positive sign of $\Delta G^{\neq}$ indicates that the degradation of the related copolymer is nonspontaneous. All E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ are positive for Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) at T_{max} which refers to the fact that the degradation is nonspontaneous while it is spontaneous at higher temperatures than T_{max} because $T_{max}\ \Delta S^{\neq}$ › $\Delta H^{\neq}$ and consequently $\Delta G^{\neq}$ is negative as readily seen in Eq.13.

Table 5. Pre-exponential factor (A), activation enthalpy ($\Delta H^{\neq}$), entropy ($\Delta S^{\neq}$) and Gibbs energy ($\Delta G^{\neq}$) of Poly(AGE-*co*-AMA) obtained by Coats-Redfern method for $\boldsymbol{F_3}$ model (main degradation stage) at 15°C/min

Stage	Symbol	Pre-exponential factor A(/min)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (kJ/mol K)	$\Delta G^{\neq}$ (kJ/mol)
Main stage	**F_3**	$1.93x10^{19}$	250	0,117	169

Table 6. Pre-exponential factor (A), activation enthalpy ($\Delta H^{\neq}$), entropy ($\Delta S^{\neq}$) and Gibbs energy ($\Delta G^{\neq}$) of Poly(AGE-*co*-MMA) obtained by Coats-Redfern method for $\boldsymbol{F_3}$ model (main degradation stage) at 15°C/min.

Stage	Symbol	Pre-exponential factor A(/min)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (kJ/mol K)	$\Delta G^{\neq}$ (kJ/mol)
Main stage	F_3	$1.08x10^{25}$	302	0.317	94

4. CONCLUSIONS

The kinetics of thermal degradation of AGE copolymers were studied and discussed. The activation energies calculated by KAS method for Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) were found to be 292±10 kJ/mol and 175±27 kJ/mol for the first stage, and 252±74 kJ/mol and 232±32 kJ/mol for the second, respectively while they were 361±1 kJ/mol and 249±61 kJ/mol for Poly(AGE-*co*-AMA) and 136±24 kJ/mol and 278±18 kJ/mol for Poly(AGE-*co*-MMA) by FWO method.

The activation energies determined by KAS and FWO methods indicate that the thermal stabilities exhibit an order of Poly(AGE-*co*-AMA)>(Poly(AGE-*co*-MMA). Poly(AGE-*co*-AMA) copolymer has significantly higher E_a value than that of Poly(AGE-*co*-MMA) probably due to crosslinking during its polymerization. Both of the thermal degradation mechanisms of the main degradation stages of Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) obtained from Coats-Redfern method seem to be a random nucleation with two nuclei on the individual particle which is known as $\boldsymbol{F_3}$ model.

All thermodynamic parameters, namely E_a, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ are shown to be positive as a result of kinetic analysis of the thermal degradation of Poly(AGE-*co*-AMA) and Poly(AGE-*co*-MMA) which consequently implies that the thermal degradation is spontaneous at higher temperatures.

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