Thermal and morphological characteristics of solution blended epoxy/NBR compound

Hamidreza Ali-Asgari Dehaghi, Saeedeh Mazinani, Davood Zaarei, Mohammadreza Kalaee, Hamed Jabari & Navid Sedaghat

Journal of Thermal Analysis and Calorimetry An International Forum for Thermal Studies

ISSN 1388-6150 Volume 114 Number 1

J Therm Anal Calorim (2013) 114:185-194 DOI 10.1007/s10973-012-2920-3





Your article is protected by copyright and all rights are held exclusively by Akadémiai Kiadó, Budapest, Hungary. This e-offprint is for personal use only and shall not be selfarchived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".



Thermal and morphological characteristics of solution blended epoxy/NBR compound

Hamidreza Ali-Asgari Dehaghi · Saeedeh Mazinani · Davood Zaarei · Mohammadreza Kalaee · Hamed Jabari · Navid Sedaghat

Received: 2 October 2012/Accepted: 18 December 2012/Published online: 17 January 2013 © Akadémiai Kiadó, Budapest, Hungary 2013

Abstract Systematic study about the effect of acrylonitrile-butadiene rubber (NBR) concentration on the fracture toughness and thermal behavior of epoxy resin is conducted in this study. NBR is solved in an aromatic hydrocarbon solvent and is added to epoxy resin. We used diethylene-teriamin as the curing agent for epoxy resin. Tensile test results, performed followed by molding procedure, show that the toughness is improved owing to the increase of rubber content. Scanning electron microscopy (SEM) and atomic force microscopy besides thermogravimetric analysis (TG) are used to investigate the epoxy/ rubber interface and chemical decomposition of the resultant mixture. The thermal behavior of cured epoxy resin was analyzed via TG instrument at different heating rates. Thermogravimetry curves showed that the thermal decomposition of epoxy system was occurred in only one stage regardless of the rubber content. The apparent activation energies of the rubber/epoxy systems containing 0, 5, and 10 phr of rubber were determined by Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose, and Friedman methods. The results prove that the thermal stability of epoxy resin was decreased with enhancing the rubber content. However, the trend of changing activation energy versus conversions is totally different followed by adding the

H. Ali-Asgari Dehaghi \cdot D. Zaarei \cdot M. Kalaee \cdot H. Jabari \cdot N. Sedaghat

Department of Polymer Engineering, Islamic Azad University, South Tehran Branch, 1777613651 Tehran, Iran

S. Mazinani (🖂)

elastomer to the system compared to neat epoxy resin. Moreover, the results obtained via our proposed facile solution blending method are compared to those of resins modified with nano-powdered elastomer.

Keywords NBR elastomer · Epoxy resin · Compound · Solution blending · Thermal degradation

Introduction

Epoxy resins are considered as one of the most important classes of thermosetting polymers and are employed as structural adhesives, matrices in fiber-reinforced composites, coatings for metals, and other engineering application. They are relatively brittle and show poor resistant against crack initiation and growth. To address this defect, resin formulators have developed a technological method that permits thermoset resins to be toughened by the addition of a second elastomeric phase [1-5]. Also, their low shrinkage upon curing (less than 0.5 %) has made them a good candidate for molding over curing process [6]. There are several approaches to enhance the epoxy resin toughness [6–12] which include: chemical modification of the epoxy backbone to make it more flexible, increasing the molecular mass of epoxy, lowering the cross-link density of matrix, incorporation of a dispersed toughener phase in the cured polymer matrix, and inclusion of inorganic fillers into the neat resin. Amongst these approaches, toughening mechanism by rubber particles has so far shown to be the most effective method. These toughening agents could include reactive or nonreactive rubber parts [8-11]. Powdered thermoset coatings are solvent free and unlike the conventional liquid coatings have zero volatile organic content (VOC) [13, 14].

Amirkabir Nanotechnology Research Institute (ANTRI), Amirkabir University of Technology, 158754413 Tehran, Iran e-mail: s.mazinani@aut.ac.ir

Author's personal copy

It is generally accepted that the degradation of epoxy resin starts by the dehydration of secondary alcoholic groups followed by hemolytic session of the formed allelic bond. Repetition of the epoxy network bond session leads to the evaporation of low molecular mass fragments; whereas, polymerization of unsaturated bonds resulting from dehydration and subsequent aromatization contributes to charring [15].

For many years, it has been well established that through different toughening mechanisms, the incorporation of a second phase of either soft or rigid fillers can confer greatly enhanced fracture toughness to epoxies. Typically, the fillers are of micron size [16] and due to their small size and large surface area, nanoparticles are unique fillers yielding totally different effects and improved physical properties compared to conventional fillers with sizes in the micrometer range. Of particular importance, nanoparticles present in the polymer must be well distributed in order to change the polymer properties. Since the thermal and thermal-oxidative stability are related to both the initial degradation temperature and the degradation rate of a polymer [17], the determination of activation energy and reaction order associated with degradation is an interesting topic.

Recently, according to Khoee et al. [18], the adhesion strength increased dramatically by addition of copoly(styrene-butylacrylate-ethylenglycoldimethacrylate) (St-BA-EGDMA) nanoparticles to pure epoxy adhesive. The highest adhesion strength was obtained in the samples containing 20 wt% elastomeric (St-BA-EGDMA) nanoparticles. It was found that reinforcement with nanoparticles improved the fracture toughness. In addition, Liu et al. [19] introduced a novel powdered rubber product in nanoscale particle size for the first time to be applied in friction materials. Since its industrialization, the novel rubber product has been already successfully applied to areas such as thermoplastics and thermosets toughening. The results of constant speed friction test and dynamometer test showed that nano powdered rubber can substantially improve the properties of friction materials. Balakrishnan et al. [20] studied the influence of both the rubber toughener and clay concentration on the morphology and mechanical properties of three-phase, rubber-modified epoxy nanocomposites. Their results showed that the tensile modulus and strength was increased and ductility was decreased with increasing the organoclay content, while rubber has the opposite effects on the properties of epoxy resin. Lee et al. [21] studied the thermal decomposition kinetics of diglycidyl ether of bisphenol A (DGEBA) with methylene di-aniline (MDA) hardener using Ozawa, Kissinger, and Friedman methods. Moreover, they studied the kinetic parameters and the results were compared. The thermal stability of the epoxy system was increased with increasing the rubber-modified MDA content.

Study the thermal degradation properties of both soft and hard thermoset resins by kinetics models has always been of great interest in literature due to the complicated structure of such systems [22–24]. In our previous work, we studied the effects of nano-CaCO₃ on morphology, cure behavior, adhesion, and hardness of polyester/epoxy systems. The most important finding based on the rheological studies was the catalytic effect of nano-CaCO₃ on cure reaction of polyester/epoxy, leading to shorter curing time. Moreover, the kinetic analyses of rheograms revealed a marked decrease in the activation energy of the cure process upon raising nano-CaCO₃ content [14].

This paper discusses the effects of adding acrylonitrile– butadiene rubber (NBR) to the epoxy resin. The objective of this study is to examine the influence of rubber concentration on morphology, toughness, and thermal properties followed by the elastomer solution blending. We used solution blending method as a replacement of micro/ nano elastomer particle addition to thermoset resin to compare the results with previous reports of micro/nano particles modification method. We examined the effect of changing the elastomer content on morphology and fracture behavior of resultant toughened epoxy systems. Also, thermal behavior of resultant compounds has been studied via thermogravimetric analysis (TG) and decomposition kinetics were studied using FWO, KAS, and Friedman methods.

Experimental

Material

The following materials were used in this study: epoxy resin based on diglycidylether bisphenol A(LY 441) obtained from Huntsman Co. Germany, and diethyleneteriamine as the curing agent of epoxy resin was also purchased from Huntsman Co., Germany. NBR with acrylonitrile content of 33 %, in powdered form was provided from Jahan Tormoz Kashan Co., Iran. We used a solvent mixture including toluene:*n*-butanol:butyl acetate (40:20:40); all purchased from Merck Co. and used as received.

Preparation of cured samples

Table 1 shows the epoxy/rubber compounds containing various amounts of rubber concentrations. NBR powder was first swelled in the solvent mixture including: toluene:*n*-butanol:butyl acetate (40:20:40). Then, epoxy resin was added to the mixture and the composition was stirred by homogenizer for 15 min at 3,000 rpm to form a stable transparent dispersion. The prepared compounds were containing 0, 5 and 10 phr of rubber in epoxy resin. Epoxy compounds were then mixed with diethyleneteriamie as curing agent (Table 1). Increasing the rubber content leads to the change of samples color from light yellow to white. The mixture was then heated up to 80 °C under vacuum to totally remove the solvent. Followed by completing compounds mixing; the mixture was poured into a silicone mold and cured at 80 °C for 2 h in an oven. The time and temperature were optimized followed by different steps to complete the curing and to reduce the porosity content caused by solvent evaporation during curing. The oven is then turned off and the samples are allowed to be slowly cooled down to the room temperature as post curing step for the samples. All samples passed the same thermal history during molding.

Morphology observation

Scanning electron microscopy (SEM) imaging was performed employing Vegall model apparatus by Tescan Co. equipped with an energy beam of 20 kV. The prepared samples were cryogenically fractured in liquid nitrogen and then coated via gold vapor deposition method using a vacuum sputter, model K450X manufactured by Emitech Co. before SEM observation. Atomic force microscopy (AFM) results were obtained using a Dualscope DS 95-200, DME and the experiments were all performed in a tapping mode. Samples for AFM were all developed on a freshly cleaved mica surface. All measurements were made at ambient temperature.

Measurement of mechanical properties

The cured specimens were approximately prepared in size of 11 mm (width) by 4.5 mm (thickness) by 5 cm (length). The tensile experiments were all conducted at room temperature at speed of 5 mm min⁻¹ employing Gotech tensile machine and stress–strain curves were obtained four times on each sample according to ASTM D638. We could calculate tensile modulus, tensile strength, fracture strain, and toughness via this method.

Thermal analysis

The thermal degradation of the blends was analyzed using STA PT1600 thermogravimetric analyzer (Germany) according to ASTM D6370 under nitrogen atmosphere.

Kinetics of non-isothermal degradation

used for all measurements.

All kinetic analyses of non-isothermal data (TG, DTG) are based on the Eq. (1) [25].

tained at 33 mL min⁻¹ and samples of ca. 20 mg were

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \beta \frac{\mathrm{d}\alpha}{\mathrm{d}T} = Af(\alpha) \mathrm{Exp}\left(\frac{-E}{RT}\right) \tag{1}$$

In Eq. (1), α is the degree of conversion; *A* is the preexponential factor; *E* is the activation energy; *R* is the gas constant; *T* is the reaction temperature; and $f(\alpha)$ is the differential conversion function and $\beta = \frac{dT}{dt} = \text{const.}$ is the linear heating rate. In Eq. (1), such a forced description is perhaps one of the reasons for obtaining activation parameters depending on degree of conversion.

Isoconversional methods

The second methods including isoconversional methods of FWO, Friedman and KAS are in fact, a "model-free" method; since they assume that in these models conversion function, $f(\alpha)$, does not change with changing heating rate for different values of α . In this method, the temperatures corresponding to fixed values of α , is measured from experiments at different heating rates β .

Friedman method (FR) [26]

The differential isoconversional method suggested by Friedman (FR method) is based on Eq. (2):

$$\mathrm{Ln}\beta\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \mathrm{Ln}A + \mathrm{Ln}f(\alpha) - \frac{E}{RT}$$
(2)

In Eq. (2), for $\alpha = \text{const.}$, followed by plotting $\text{Ln}(\beta \frac{d\alpha}{dt})$ versus (1/*T*), obtained from the curves recorded at several heating rates, a straight line is obtained whose slope allows evaluation of the activation energy.

Flynn-Wall-Ozawa method (FWO) [27]

The isoconversional integral method suggested independently by Flynn and Wall and Ozawa [28] uses Doyle's

 Table 1
 Samples specification and preparation condition

Sample	NBR/phr three samples	Curing agent/phr	Mixing time/min	Mixing speed/rpm	Curing temperature/°C
Epoxy/NBR	0, 5, 10	15	15	3,000	80

approximation [29] of the temperature integral. This method is based on the Eqs. (3) and (4).

$$\ln\beta = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.053\left(\frac{E}{RT}\right)$$
(3)

where

$$g(\alpha) = \int_{0}^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} \tag{4}$$

where in Eq. (3) for $\alpha = \text{const.}$, the plot of $\ln\beta$ vs. (1/*T*) obtained from the curves recorded at several heating rates, should give a straight line whose slope allows evaluation of the activation energy.

Kissinger-Akahira-Sunose method (KAS) [30, 31]

Equation (5) shows the conversional integral method based on the Coats–Redfern approximation [32] of the temperature integral.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_{g}(\alpha)}\right) - \frac{E}{RT}$$
(5)

In Eq. (5), for $\alpha = \text{const.}$, the plot of $Ln\left(\frac{\beta}{T^2}\right)$ vs. (1/*T*), obtained from curves recorded at several heating rates

Fig. 1 Scanning electron microscopy images of the fractured surface of compounds containing: **a**, **b** 5 phr; and **c**, **d** 10 phr of NBR results in a straight line whose slope could be used to evaluate the activation energy.

Results and discussion

Morphological observation

SEM was used in order to study the effect of NBR particles on final epoxy morphological structure (Fig. 1). Figure 1a, b shows the fracture surface of 5 phr rubber-filled epoxy, and Fig. 2c, d shows the fracture surface of 10 phr rubber-filled epoxy at different magnifications. The observations show that large changing occurred in the toughness with increasing the rubber content due to the reduction in cracks in related samples. In addition, Fig. 1 shows that a large number of holes were developed where the rubber content is decreased. The main reason for this criterion is that more solvent is remaining in the material after rubber feeding to the solvent and the epoxy matrix is well homogenized with rubber; since the holes are developed by the solvent evaporation and the elastomer is remained unchanged in the system.

3D-AFM representation of treated sample films (Fig. 2) shows a slightly increase in surface roughness followed by





Table 2 Tensile parameters of compounds after curing

Sample	Tensile modulus/MPa	Tensile strength/MPa	Strain at break/%	Fracture energy/mJ
Pure epoxy	714 ± 5	47.5 ± 0.7	4.2 ± 0.01	4,367 ± 55
Epoxy + 5 phr	250 ± 10	12 ± 0.2	8.5 ± 0.04	1216 ± 30
Epoxy + 10 phr	150 ± 8	10 ± 0.07	18 ± 1	485 ± 25

elastomer addition. Compounds containing NBR content of 5 (Fig. 2a) and 10 phr (Fig. 2b) are not totally smooth as depicted in 3D representation of the rubber/epoxy compound surface. The related root-mean square (R_q) parameter of the compounds could also come as evidence that surface roughness is improved by the rubber content. The relation observed between rubber content and surface roughness is a proof that the holes and surface roughness are developed by rubber particles and they are not only the result of solvent evaporation of compounds. These show a micrograph of a fractured rubber modified epoxy sample, and this phenomenon can be described by different methods.

Since the images are obtained from the fractured surface of compound, it is more probable to be the effect of elastomeric parts. Holes in the stress whitened region presumably result from the rupture of elastomeric particles. Under tensile stress, the rubber particle should contract laterally more than the matrix but proper bonding between the rubber particle and matrix (observed by homogenous solution mixing in our solvent) prevents the rubber particle from soothe operation and it causes developing a stress on the rubber particle. The rubber particle tears and releases this stress, resulting in removal of rubber particles which appears as depressions on the fractured surface. The cavitation in the rubber particle makes it easy to see the two phase (rubber particles dispersed in epoxy matrix) morphology [20]. Changing the holes content and roughness of fractured with rubber increment in samples thickness could justify the presence of rubber particles in holes as separated phase after curing. The holes are mostly formed on the surface and they are not depending on rubber content. In addition, such holes in the system could cause serious defects and reduction in elongation at break of the samples compared to neat epoxy which is not the case in our system of study (Table 2). Rubber modification has increased the elongation at break which is the evidence of rubber incorporation and toughness improvement.

Secondly, the reactive liquid rubbers, usually carboxylterminated nitrile butadiene copolymers (HyproTM CTBNs) might react with excess of epoxy resin. The resulting epoxy mixtures are then used to formulate the adhesive, the impregnating, or laminating resin system. During curing a phase separation occurs and small rubber domains are formed. The toughening mechanisms of this secondary rubbery phase are well understood [21], and we do not mean to focus on co-curing or toughness mechanisms development in this paper. However, these phenomena are the most probable toughening mechanism here and they are probable to occur during curing in the system of our study.

Effect of rubber content on mechanical characteristics

Figure 3 shows the comparison of tensile behavior of cured specimens containing different rubber contents including: 0, 5, and 10 phr rubber content. This figure represents stress versus strain curves in the experiment for three different samples tested at each loading fraction in our study.

The addition of NBR to epoxy resin leads to tensile modules and strength changing. Increasing in the amount of rubber from 0 to 5 and from 5 to 10 phr caused the decrease of tensile module (Table 2).

In the case of tensile strength, the trend is totally different and increasing in the amount of rubber content from 0 to 5 and from 5 to 10 phr causes decrease in tensile strength from 47.5 to 12 and from 12 to 10 MPa, respectively.

The mechanism for toughening indicates that the rubber particles cause cavitation and thus act as initiator for yielding in the epoxy matrix [16, 33]. It means that the previously blended elastomer changed to fine dispersed particles and it results in cavitations and strong toughening



Fig. 3 Stress-strain curves of compounds after curing

phenomenon. Since, increasing the rubber content and changing the rubber particles sizes to finer ones, has caused decreasing the cracks and cracks propagation (Fig. 1).

Analysis of thermal properties

TG curves were employed to evaluate the thermal stability of compounds. Figure 4 shows the TG plots of materials, recorded under nitrogen atmosphere. As shown, a decrease in initial decomposition temperature of epoxy networks was observed followed by incorporation of rubber into the resin system. The composites exhibited substantial decrease especially in initial decomposition temperature and the maximum decomposition temperature, and only a slight increase in the final decomposition temperature was recorded followed by rubber incorporation to the system. $T_{\rm f}$ of higher value is probably due to the decomposition of the physically cross-linking moiety of elastomer particles with epoxy resin matrix (Table 3). The temperature at which 50 wt% mass loss occurred (T_{50}) for the samples containing 5 and 10 wt% of rubber content, was also lower than that of the corresponding unmodified epoxy resin. It suggests that the presence of rubber could result in lower thermal stability than neat epoxy material in spite of more toughening behavior observation.

Activation energy (E_a) calculated from three models varies greatly with conversion. If E_a does not vary greatly with conversion, it is possible to describe the whole reaction interval by a single kinetic model even if the real reaction mechanism is complex. Therefore, we must use different models for this analysis. The activation energy calculated from models based on a single heating rate showed smaller amounts compared to models based on multiple rates and they are employed for our analysis. To compare the kinetic parameters, the results of the analytical methods are summarized in Table 4. Whereas three different models including KAS's, FWO's, and Friedman's values are reported here; the activation energies obtained from KAS, FWO, and Friedman methods show almost the same value.

Figure 4 also shows the comparison of derivative thermogravimetry (DTG) curves at the heating rate of 20 °C min^{-1} . DTG curves shifted to lower temperatures and the decomposition starting temperature appeared at a lower point with increasing the rubber content. TG curves showed that the thermal decomposition of the epoxy system occurred in one stage regardless of the rubber content. The apparent activation energies for the rubber/epoxy system containing 0, 5, and 10 phr of rubber, were determined by FWO, KAS, and Friedman methods. The thermal stability of the epoxy system reduced with increasing the content of rubber that led to a decrease in activation energy. As a result, a functional dependency of apparent activation energy on conversion was obtained, which can indicate the complexity of the reaction mechanism. Integral isoconversional methods, such as KAS, FWO are suited for the analysis of TG curves since they do not require the experimental data to be differentiated beforehand [26].

The activation energies of Friedman (Fig. 5) and FWO (The curves are not shown here) methods for the thermal decomposition are determined from the slope of $Ln(\beta)$ vs. 1,000/*T*. Friedman model curves are shown in Fig. 5, and we avoid showing the detailed modeling procedure of other two methods here since they are given in Table 4 in details. The activation energies of KAS method for thermal decomposition are determined from the slope of $Ln(\frac{\beta}{T^2})$ vs. 1,000/*T* (the curves are not shown here). It is apparent that the data-points are well fitted to the straight lines





 Table 3 Thermal properties of modified and unmodified epoxy resins obtained from TG and DTG curves

Table 4	Activation	energies	determined	by	Friedman,	F-W-O, a	nd
KAS met	thods						

Sample/phr	$T_{\rm i}/^{\rm o}{\rm C}^{\rm a}$	$T_{50}/^{\mathrm{o}}\mathrm{C}^{\mathrm{b}}$	$T_{\rm max}/{\rm ^oC^c}$	$T_{\rm f}/^{\circ}{\rm C}^{\rm c}$
0	185	370	385	480
5	175	360	377	490
10	170	350	370	498

^a Initial decomposition temperature is the temperature at which initial loss of mass was observed

 b Temperature at which 50 % mass loss was recorded by DTG with heating rate of 20 oC min $^{-1}$ under N_2 atmosphere

 c Temperature at which maximum mass loss was recorded by DTG with a heating rate of 20 oC min $^{-1}$ under N_2 atmosphere

 d Temperature at which final mass loss was recorded by TG with heating rate of 20 oC min $^{-1}$ under N_2 atmosphere

(r > 0.99). Nearly, the same slopes over the whole α range of 0.4–0.8 indicate that the same reaction mechanism is acting on decomposition of the cross-linked chains with constant activation energy. In all compounds, the determined activation energies were decreased with increasing the conversion.

The resulting dependency of E_a on α for all investigated system is displayed in Fig. 6. It can be observed that E_a of modified epoxy system was decreased compared to neat resin (Table 4). Obviously, the kinetic parameters calculated by different methods did not show any significant difference. However, a slight disagreement between the results obtained from Friedman and Kissinger models might be due to the different mathematical approaches used to calculate the parameters. Therefore, the small differences among r values, which are mainly due to inherent experimental errors, cannot be used to discriminate amongst the kinetic models. For a given value of α , E values of Friedman is almost the same as E values evaluated by the integral isoconversional methods in this study.

Elastomers generally have a low thermal stability and the addition of elastomer to the epoxy with high thermal stability makes a reduction in the thermal properties [34]. It is against to the results reported by Ma et al. [34], that the slope of elastomeric nanoparticle (ENP)-modified phenolic resin (PR) increased with increasing the ENP content, and their activation energies of curing reaction were also increased. The values of activation energies fall between those for homolytic scission and dehydration of epoxy resins, which is probably caused by the complete reaction of epoxy groups with NBR. These results are arguments for the quasichemical approximation according to which the degradation of a mechanical property of a polymeric material is due to a chemical reaction that can be described by equations from chemical kinetics. However, the exact physical meaning of the kinetic parameters is not clear yet in the literature; since, the exact mechanisms of thermal

Conversion α		Epoxy + 0 % NBR							
		Friedman			F-W-O			KAS	
		Ε	r	-	E	r	_	Ε	r
0.4		210.2	0.9995	5	211.1	0.998	5	211.9	0.9888
0.45		220.5	0.9953	3	221.4	0.993	7	222.3	0.9857
0.5		225.1	0.9927	7	226.4	0.994	5	227.3	0.9845
0.55		222.8	0.9978	8	223.2	0.997	3	224.1	0.9975
0.60		217.2	0.9898	8	222.2	0.995	8	222.7	0.9968
0.65		211.2	0.9997	7	218.1	0.999	4	218.5	0.9969
0.70		193.8	0.9939)	212.2	0.999	5	212.5	0.9956
0.75		193.8	0.9942	2	194.7	0.997	8	196.1	0.9988
0.8		178.6	0.9847	7	179.5	0.998	9	179.9	0.9991
Epoxy + 5	% I	NBR							
Friedman			F-W-	-0			K	AS	
Ε	R		Ε		r		E		r
240.9	0.9852		241.7		0.9745		24	2.6	0.9884
219.69	0.9	9815	220.5		0.9867		22	1.4	0.9991
196.2	0.9877		197.6		0.9889		19	8.4	0.9841
179.9	0.9	9832	181.7		0.9793		18	2.1	0.9849
163.2	0.9871		164.9		0.9978		16	5.4	0.9934
151.2	0.9848		152.4		0.9937		153.8		0.9757
150.3	0.9	9730	151.1		0.98	76	15	2.5	0.9867
154.7	0.9863		155.9		0.9797		156.5		0.9888
164.3	0.9869		165.5		0.9874		166.1		0.9885
Epoxy + 1	0 %	NBR							
Friedman			F-W-	0			KA	4S	
E	R		E		r		E		r
181.7	0.99	989	183.9		0.984	46	18	4.3	0.9846
176.1	0.99	975	177.9		0.9845		178.3		0.9845
164.6	0.99	968	166.8		0.9888		167.7		0.9888
150.5	0.99	986	152.7		0.9868		153.5		0.9845
137.7	0.99	943	139.8		0.98	88	140.7		0.9943
126.9	0.99	935	128.6		0.998	85	12	9.1	0.9935
127.1	0.99	988	128.3		0.98	57	7 128.8		0.9988
131.1	1.1 0.9991		131.5		0.99	92	131.9		0.9991
137.3	0.99	982	135.9		0.998	87	13	6.8	0.9845

decomposition of thermoset resins cannot be easily defined. While the physical meaning of all the kinetic parameters for thermoplastics are easily interpreted because the apparent mass loss is directly related to the mechanism of thermal decomposition, which is the emission of gaseous products after the chemical session. However, for crosslinked thermoset polymers, the decomposition follows **Fig. 5** Plots of Friedman method for epoxy/rubber system at: **a** 0, **b** 5, and **c** 10 phr rubber content at various fixed conversions



Fig. 6 Plots of activation energy versus conversion for neat epoxy and compounds calculated by: a Firedman, b FWO, and c KAS methods

several processes, each with its own kinetic parameters. Therefore the kinetic parameters are somewhat apparent values, and there are some differences according to various analytical methods. Increasing the activation could be related to two main reasons as previously reported in the literature. First, it could be increased followed by the cross-links formation between epoxy and rubber phase or due to the humidity presence in the sample during the reaction [21]. Second, the activation energy could be increased due to the reaction of amine group with the curing agent [34], which is observed at the end of the curves in our system of study.

Conclusions

The influence of NBR as epoxy resin toughener on morphology, tensile and thermal degradation properties of this resin was studied. NBR was solved in a suitable solvent and then was added to epoxy resin. Followed by examining the fracture behavior, we obtained a large changing in epoxy toughness with increasing the rubber content. In the case of tensile strength, the trend was different from modules behavior, and the addition of rubber caused decrease in tensile strength. TG curves showed that the thermal decomposition of the epoxy system was occurred in only one stage regardless of rubber-modified epoxy content. TG and data were analyzed kinetically by three different methods, each of which gave different apparent kinetic parameters. The thermal stability of the epoxy system reduced with increasing the rubber content due to the NBR presence which might be the reason of rubber existence as a part of blend with lower thermal stability component. We merely observed an increase in thermal stabilities of the blended samples only as high conversion ratios which might be due to the epoxy/NBR cross-link formation.

References

- Lee H, Neville K. Handbook of epoxy resins. New York: McGraw-Hill; 1967.
- Ramos VD, Costa HM, Soares VLP, Nascimento RSV. Modification of epoxy resin: a comparison of different types of elastomer. Polym Test. 2005;24:387–94.
- 3. Celikbilek C, Akovoli G, Kaynak C. Modification of epoxy by a liquid elastomer and solid rubber particles. Polym Bull. 2004;51: 429–35.
- Riew CK. Rubber-toughened plastics. In: Advances in chemistry series 222. Washington, DC: American Chemical Society; 1989.
- Kinloch AJ, Shaw SJ, Tod AD, Hunston DL. Deforming and fracture behavior of a rubber-toughened epoxy: 1. Microstructure fracture studies. Polymer. 1983;24:1341–54.
- Tai RCL, Szklarska-Smialowska Z.Effect of fillers on the degradation of automotive epoxy adhesion in aqueous solutions. J Mater Sci. 1993;28:6199–204.
- Jin FL, Park SJ. Thermal stability of trifunctional epoxy resins modified with nanosized calcium carbonate. Math Sci Eng A. 2008;478:334–8.
- Unnikrishnan KP, Thachil ET. Toughening of epoxy resins. Des Mon Polym. 2006;9:129–52.

- Ratna D. Modification of epoxy resins for improvement of adhesion: a critical review. J Adh Sci Tech. 2003;17:1655–68.
- Hedia HS, Allie L, Ganguli S, Aglan H. The influence of nano adhesives on the tensile properties and mode-I fracture toughness of bonded joints. Eng Frac Mech. 2006;73:1826–32.
- Dodiuk H, Keing S, Blinsky I, Dotan A, Buchman A. Nano tailoring of epoxy adhesive by polyhedral-oilgomeric-silsesquioxanes (POSS). Int J Adh Adh. 2005;25:211–8.
- Zhai LL, Ling GP, Wang YW. Effect of nano-Al₂O₃ on adhesion strength adhesive and steel. Int J Adh Adh. 2007;28:23–8.
- Papasavva S, Kia Sh, Claya J, Gunther R. Characterization of automotive paints: an environment impact analysis. Pro Org Coat. 2001;43:193–206.
- 14. Kalaee M, Akhlaghi SH, Nouri A, Mazinani S, Mortezaei M, Afshari M, Mostafanezhad D, Allahbakhsh A, Dehaghi HA, Amirsadri A, Gohari DP. Effect of nano-sized calcium carbonate on cure kinetics and properties of polyester/epoxy blend powder coatings. Pro Org Coat. 2011;71:173–80.
- Levchik SV, Camino G, Luda MP, Costa L, Costes B, Henry Y, Morel E, Muller G. Mechanistic study of thermal behavior and combustion performance of epoxy resins: I homopolymerized TGDDM. Polym Adv Tech. 1994;6:53–62.
- Khoee S, Mahdavian AR, Bairamy W, Ashjari M. An investigation into the improvement of adhesive strength of polyimides by incorporation of elastomeric nanoparticles. J Col Int Sci. 2009;336:872–8.
- Salin IM, Seferis JC. Kinetic analysis of high resolution TGA variable heating rate data. J App Pol Sci. 1993;47:847–58.
- Khoee S, Hassani N. Adhesion strength improvement of epoxy resin reinforced with nanoelastomeric copolymer. Mat Sci Eng A. 2010;527:6562–7.
- Liu Y, Fan Z, Ma H, Tan Y, Qiao J. Application of nano powdered rubber in friction materials. Wear. 2006;261:225–9.
- 20. Balakrishnan S, Start PR, Raghavan D, Hudson SD. The influence of clay and elastomer concentration on the morphology and fracture energy of preformed acrylic rubber dispersed clay filled epoxy nanocomposites. Polymer. 2005;46:11255–62.
- Lee JY, Shim MJ, Kim SW. Thermal decomposition kinetics of an epoxy resin with rubber-modified curing agent. Appl Polym Sci. 2001;81:479–85.
- Maciejewski H, Dabek I, Fiedorow R, Dutkiewicz M, Majchrzak M. Thermal stability of hybrid materials based on epoxy functional (poly)siloxanes. J Therm Anal Calorim. 2012;110:1415–24.
- Calvo S, Escribano J, Prolongo MG, Masegosa RM, Salom C. Thermomechanical properties of cured isophtalic polyester resin modified with poly(e-caprolactone). J Therm Anal Calorim. 2011;103:195–203.
- Kalaee MR, Akhalaghi S, Mazinani S, Sharif A, Jarestani YC, Mortezaei M. Effect of ZnO nanoparticles on kinetics of thermal degradation and final properties of ethylene–propylene–diene rubber systems. J Therm Anal Calorim. 2012;110:1407–14.
- Paulik F. Special trends in thermal analysis. J Therm Anal Calorim. 1995;45:1605–6.
- Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry, application to a phenolic plastic. J Polym Sci Polym Sym. 1964;6:183–95.
- 27. Flynn JH, Wall LA. General treatment of the thermogravity polymers. J Res Nat Bur Stan-A Phys Chem. 1966;70A:487.
- Doyle C. Estimating isothermal life from thermogravimetric data. J Appl Polym Sci. 1962;6:639–42.
- 29. Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem. 1957;29:1702.
- Akahira T, Sunose T. Report of the Chiba institute technology. Trans Res. 1971;16:22.
- Coats AW, Redfern JP. Kinetic parameters from thermogravimetry. Nature. 1964;201:68–9.

- 32. Vaia RA, Giannelis EP. Polymer nanocomposites: status and opportunities. MRS Bull. 2001;399:394–401.
- Ozawa T. Kinetic analysis of derivation curves in thermal analysis. J Therm Anal Calorim. 1970;2:301–24.
- Ma H, Wei G, Liu Y, Zhang X, Gao J, Huang F, Tan B, Song Z, Qiao J. Effect of elastomeric nanoparticles on properties of phenolic resin. Polymer. 2005;46:10568–73.