Thermal decomposition kinetics of benzofuran derived polymer/organosilicate nanocomposites

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Abstract

Benzofuran derived polymer poly(2-(5-bromo benzofuran-2-yl)-2-oxoethyl methacrylate)/organically modified montmorillonite nanocomposites were prepared via in situ polymerization technique. Vinyl benzyl dimethyl hexadecyl ammonium chloride was used as organic-modifier. X-ray diffraction analysis showed the silicate dispersion in the polymer matrix with an exfoliated structure. The thermal stabilities of nanocomposites were increased with loading organosilicate in the polymer matrix. The decomposition temperature of 5 wt% organosilicate nanocomposite at 10% weight loss was approximately 14 °C higher than that of pure polymer. Kinetic analysis of the decomposition process in nanocomposites was evaluated from dynamic experiments by means of Flynn-Wall-Ozawa and Coats-Redfern methods within 12% - 22% decomposition conversion range. Introduction of the silicate phase in polymer enhanced the apparent activation energy from 163.31 kJ/mol to 195.28 kJ/mol. The mechanism of thermal degradation for pure polymer in this conversion range probably followed a deceleration type phase boundary controlled reaction (R_3) , whereas in case of nanocomposites, it shifted to dimensional diffusion type (D_n) .

Keywords: Activation energy; benzofuran; polymer/silicate nanocomposites; reaction mechanism; thermal decomposition kinetics.

1. Introduction

Investigation of thermal properties of polymeric materials is very important and required for many applications (Hu *et al.*, 2004). As is well known, thermal stabilities of polymers depend on various factors, such as the structures of polymer main chain or its side groups, thermoplastic or thermosetting shapes, amorphous or crystalline properties, additive sand fillers, etc. One of the best methods to improve thermal properties of polymeric materials is the introduction of inorganic nanoparticles in the polymeric matrix resulting in the formation of polymer/inorganic nanocomposites (Li *et al.*, 2006). In these inorganic nanoparticles, clay is generally preferred for the synthesis of polymer nanocomposites due to its some excellent properties (Panwar

et al., 2011). The extent of separation of the silica layers of the clay particles is quite important as well distributed nanoparticles may enhance the thermal properties of the polymeric materials (Li *et al.*, 2006; Lee *et al.*, 2006; Garcia *et al.*, 2007). Several mechanisms have been proposed to describe the enhancement in the thermal stability of polymers on the introduction of clay nanoparticles (Leszczyńska *et al.*, 2007; Benhacine *et al.*, 2014). Especially, the barrier effect of clay layers is an important reason in these enhancements because, by the thermal decomposition process, a polymeric-clay residue accumulates on the surface of the polymer and provides the mass and heat transfer barrier (Li *et al.*, 2006; Gilman *et al.*, 2000; Vyazovkin *et al.*, 2004). Thermal degradation kinetics data generally show that a positive correlation exists between the thermal stability and activation energy for thermal decomposition due to the barrier effect of nanoclay layers (Hu *et al.*, 2004; Li *et al.*, 2006; Leszczyńska *et al.*, 2007; Benhacine *et al.*, 2014; Bourbigot *et al.*, 2004).

In the heterocyclic compounds, benzofurans have drawn considerable attention in recent years due to their excellent properties for various applications such as physiological (Katritzky *et al.*, 1997), pharmacological (Polshettiwar & Varma, 2007), optical (Koca *et al.*, 2004), electrochemical (Xu *et al.*, 2005) and thermal (Koca *et al.*, 2012) properties. Similar improvements or applications of these compounds may be seen in polymer science and technology. Different benzofuran derivative polymers have been successfully synthesized and characterized by various methods in recent years (Banihashemi & Abdolmaleki, 2004; Pokladko *et al.*, 2008; Zhang *et al.*, 2009).

Although there are many studies based on common polymer nanocomposites as partly mentioned above, it seems that no attention has been paid for the preparation and investigation of thermal degradation kinetics of benzofuran containing polymers/ organosilicate nanocomposites according to our literature knowledge. The main objective of present study is to investigate the influence of adding organosilicate on the thermal decomposition kinetic parameters and solid state decomposition mechanisms of poly(2-(5-bromo benzofuran-2-yl)-2-oxoethyl methacrylate)/ organosilicate nanocomposites. Under non-isothermal heating conditions, the influence of organosilicate on the thermal stabilities of this polymer is studied by means of thermogravimetric analysis (TGA). A positive relation between the amount of added organosilicate phase and activation energies of nanocomposites was observed from the results of the thermal decomposition kinetic analysis.

2. Experimental

2.1. Materials

Vinylbenzyl chloride, dimethyl hexadecylamine, and pristine montmorillonite (MMT) silicate (K10, CEC = 119 meq/100 g) were obtained from Sigma-Aldrich. Benzoyl peroxide (BPO) purchased from MERCK and purified by recrystallization

from ethanol. 2-(5-bromo benzofuran-2-yl)-2-oxoethyl methacrylate monomer was synthesized and characterized according to reference (Koca et al., 2012). Vinyl benzyl dimethyl hexadecyl ammonium chloride (VHAC) was synthesized by the quaternarization reaction of vinyl benzyl chloride with dimethyl hexadecyl amine (Fu & Outubuddin, 2001). For preparation of organomodified silicate (OVHAC), pristine motmorillonite (1.5 g) was mixed in 750 ml of distilled water. After stirring for 12 h at ambient temperature, an aqueous solution of VHAC (0.84 g) was added to this suspension and stirred for 24 h. The organically modified silicate was filtered and washed with distilled water and dried. OVHAC was ground with a mortar and a pestle, and particles with the size 21 micron were collected to prepare poly(BOEMA)/ silicate nanocomposites (Kurt & Koca, 2015). For this purpose, BOEMA monomer (1.00 g) and its matching amounts of organomodified silicate (1%, 3% and 5%) were dispersed in 3 mL of 1,4-dioxane, and stirred by a magnetic stirrer for 24 h at ambient temperature. Then, benzoyl peroxide initiator (1 wt% of monomer) was added to this dispersion and treated with nitrogen for 15 minutes. These mixtures were immersed in an oil bath at 65 °C and stirred for 12 h. After polymerization reaction, the polymer/ silicate nanocomposites were isolated by precipitation in excess ethyl alcohol, filtered and dried.

2.2. Instrumental techniques

A Perkin Elmer FTIR spectrometer model Spectrum 100 was used to characterize the nanomaterials. XRD patterns were recorded under air at room temperature using RigakuRadB-DMAX II X-Ray Diffractometer equipped with a Cu-K α radiation ($\lambda = 0.15418$ nm) and Ni filter. Thermogravimetric analysis was performed on a Seiko SII 7300 TG/DTA undernon-isothermal heating conditions from ambient temperature to 500 °C at the heating rates of 5, 10, 15 and 20 °C/min in an inert argon atmosphere.

3. Results and discussion

FTIR spectrum of VHAC intercalating agent is shown in Figure 1(a). The absorptions at 3086-2850 cm⁻¹ are attributed to aromatic and aliphatic C-H stretching. At 1630 cm⁻¹ and at 1612 cm⁻¹ bands are characteristic of the aliphatic and aromatic C=C stretching vibrations, respectively. Figure 1(b) shows the most characteristic vibration bands of Na-MMT silicate, which are at 3624 cm⁻¹ (O–H stretching), 1024 cm⁻¹ (Si–O stretching), 916 cm⁻¹ (Al-OH deformation) and 623 cm⁻¹ (Al–O-Si deformation) bands (Madejova & Komadel, 2001; Madurai *et al.*, 2011).

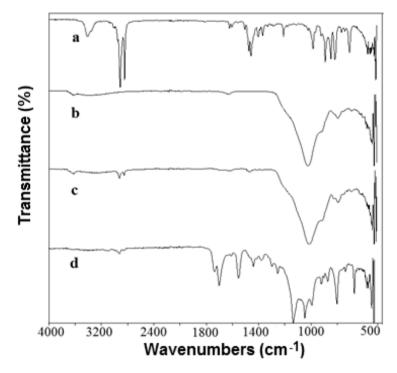


Fig. 1. FTIR spectra of (a) VHAC, (b) Na-MMT, (c) OVHAC, (d) poly(BOEMA)/OVHAC:5%

FTIR spectrum of OVHAC was illustrated in Figure 1(c). This spectrum has two different signal groups; one of them characterizes the MMT units (the most characteristics are 3603 cm⁻¹ O-H stretching, 1014 cm⁻¹ Si-O stretching), and another characterizes the VHAC intercalating agent units (the most characteristics are 3086-2850 cm⁻¹ aromatic-aliphatic C-H stretching, 1630 and 1612 cm⁻¹ aliphatic and aromatic C=C stretching vibrations). This spectrum indicates that the organic modification of MMT silicate with VHAC intercalating agent is well performed (Zhang et al., 2003). For comparison, only FTIR spectrum of the poly (BOEMA)/OVHAC:5% nanocomposites (Figure 1d) is given in the text, because of its similarity to other nanocomposites spectra. In this figure, the characteristic bands for both polymeric and organosilicateunits are also available. The most characteristic bands observed for poly(BOEMA) units are seen in 3127-2992 cm⁻¹ (aromatic and aliphatic C-H stretching vibrations), 1703 and 1738 cm⁻¹ (ketone and ester carbonyls stretching). On the other hand, except these bands, the vibrations especially observed at 1040 cm⁻¹ (broadly) and 914 cm⁻¹ (strong) are characteristics for the Si-O stretching and Al-OH deformation. These results show that the organomodified silicate exists in polymer matrix as reported by Krishna & Pugazhenthi (2011).

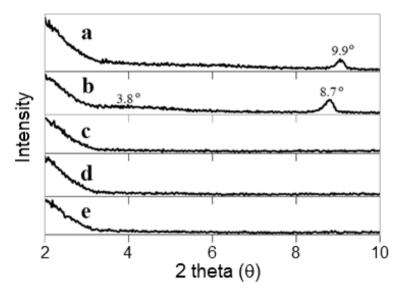


Fig. 2. XRD curves of (a) Na-MMT, (b) OVHAC, (c) poly(BOEMA)/OVHAC:1%, (d) poly(BOEMA)/ OVHAC:3%, (e) poly(BOEMA)/OVHAC:5%

The XRD patterns of nanocomposites are shown in Figure 2. The diffraction peak of pristine MMT (Figure 2a) is at about 9.9° (d = 0.89 nm). This value is shifted to lower values by organically modification. In Figure 2(b), two diffraction peaks are seen at about 3.8° (d = 2.32 nm, broadly) and about at 8.7° (d = 1.02 nm). These results confirm that VHAC has intercalated between the silicate galleries because the basal spacing of organosilicate galleries is expanded compared to pristine silicate (Fan *et al.*, 2003). The XRD curves of polymer/silicate nanocomposites have no characteristic MMT peaks. All diffraction peaks completely disappeared in the testing range, as it can be seen in Figures 2(c-e). In this perspective, it can be easily said that the organosilicate (OVHAC) is likely dispersed in poly(BOEMA) polymer matrix as exfoliated type (Krishna & Pugazhenthi, 2011).

Table 1. Thermal decomposition characteristics of nanocomposites at the heating rate of 10 °C/	min
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Polymer	T _a (⁰ C)	T _b (⁰ C)	%Weight loss at 300 ^o C	%Weight loss at 350 °C	%Weight loss at 450 ^o C		
poly(BOEMA)	254	371	31.1	46.5	68.1		
poly(BOEMA)/OVHAC:1%	259	380	28.0	44.6	67.0		
poly(BOEMA)/OVHAC:3%	263	401	21.3	40.7	60.6		
poly(BOEMA)/OVHAC:5%	268	457	20.0	32.8	48.7		
T_a and T_b : temperatures at 10% and 50% weight losses, respectively							

Thermal stabilities of polymer/silicate nanocomposite samples were determined by thermogravimetric analysis (TGA) method. TGA curves of nanocomposites at different heating rates are illustrated in Figure 3. As the heating rate is increased, the initial decomposition temperatures also increase to higher temperatures for all nanocomposites. TGA thermograms at 10 °C/min were chosen to compare the influence of organosilicateon the thermal stabilities of nanocomposites. Their results are given in Table 1. It was observed from Table 1 that the peak temperatures for all samples shifted to higher values with increasing heating rate as reported for various polymeric systems (Kurt, 2009; Li et al., 2004; Kurt & Koca, 2014). Also, Table 1 clearly demonstrated that the thermal decomposition temperatures of poly(BOEMA)/ organosilicate nanocomposites were increased by loading organosilicate. When the 10% weight loss and 10 °C/min heating rate were chosen for comparison of thermal stabilities of nanocomposites, thermal decomposition temperatures for poly(BOEMA) and poly(BOEMA)/OVHAC (1%, 3% and 5%) nanocomposites were measured to be 254 °C, 259 °C, 263 °C and 268 °C, respectively. These results showed that thermal decomposition temperature of poly(BOEMA)/organosilicate nanocomposites were higher than that of pure poly(BOEMA) about 5-14 °C at 10% weight loss. Similar results relating to increasing thermal decomposition temperatures of polymer silicate nanocomposites with organosilicate loading are also reported by some workers (Hu et al., 2004; Leszczyńska et al., 2007; Vyazovkin et al., 2004; Bourbigot et al., 2004).

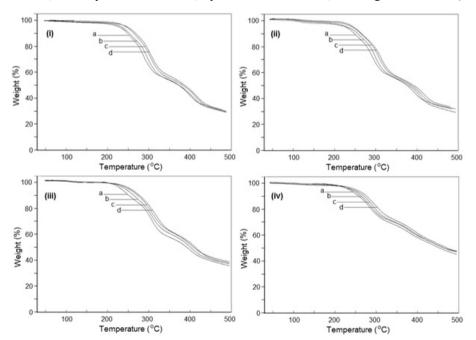


Fig. 3. TGA curves of nanocomposites (i) poly(BOEMA), (ii) poly(BOEMA)/OVHAC:1%, (iii) poly(BOEMA)/OVHAC:3%, (iv) poly(BOEMA)/OVHAC:5% at different heating rates: (a) 5 °C/min, (b) 10 °C/min, (c) 15 °C/min, (d) 20 °C/min

In case of thermal decomposition of materials, degradation process follows either a sigmoidal process or a deceleration process. Different expressions of integral function of conversion for thermally stimulated solid-state reaction mechanisms are well known in literature (Fraga & Nunez, 2001; Kaya *et al.*, 2012). These functions can be applied to thermogravimetry to estimate the thermal degradation mechanism of nanomaterials. Kinetic analysis of the decomposition process in poly(BOEMA)/ organosilicate nanocomposites was evaluated from dynamic experiments by means of Flynn-Wall and Ozawa (Flynn & Wall, 1966; Ozawa, 1986) and Coats-Redfern (Coats & Redfern, 1964) methods. The Flynn-Wall and Ozawa method is one of the integral methods to determine the activation energy without knowledge of reaction order. This method is used to determine the activation energy related conversion range on the basis of following equation:

$$\log \beta = \log \left[\frac{AE}{g(\alpha)R} \right] - 2.315 - \frac{0.457 \text{ E}}{\text{RT}}$$
(1)

where $g(\alpha)$ is the integral function of conversion, β is the heating rate, A is the preexponential factor, E is the activation energy, R is the ideal gas constant and T is the temperature. E can be calculated from the slope of the plot of log β versus 1000/*T* for a constant weight loss, which is equal to (-0.457E/R). The correlation between log β and 1000/*T* was linear. Log β versus 1000/*T* plots driven from Equation 1 were shown in Figure 4. Thermal decomposition activation energies of nanomaterials were calculated by using Flynn-Wall and Ozawa method between the conversions 12% and 22%.

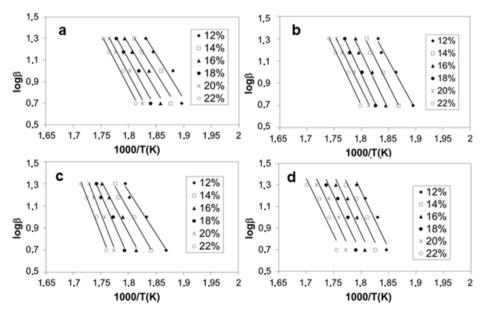


Fig. 4. Flynn-Wall-Ozawa plots of (a) poly(BOEMA), (b) poly(BOEMA)/OVHAC:1%, (c) poly(BOEMA)/OVHAC:3%, (d) poly(BOEMA)/OVHAC:5%

The investigation of all the figures (Figure 4a-d) shows that the fitting straight lines for each conversion is nearly parallel. This indicates that the applicability of Flynn-Wall and Ozawa method to the nanomaterials within this conversion range may be valid. Table 2 shows the decomposition activation energies of poly(BOEMA)/ organosilicate nanocomposites for various conversions. The mean activation energies for poly(BOEMA) and its 1%, 3%, 5% organosilicate nanocomposites were determined as 163.31 kJ/mol, 179.45 kJ/mol, 189.64 kJ/mol and 195.28 kJ/mol, respectively. These results concluded that the poly(BOEMA)/organosilicate nanocomposites had higher activation energies and thermal resistance compared to pure poly(BOEMA). The decomposition activation energies of nanocomposites also increased with organosilicate loading.

	Poly(BOEMA)		Poly(BOEMA)/ OVHAC:1%		Poly(BC OVHA		Poly(BOEMA)/ OVHAC:5%		
α	E (kJ/mol)	r	<i>E</i> (kJ/mol)	r	E (kJ/mol)	r	<i>E</i> (kJ/mol)	r	
0.12	150.90	0.9242	160.87	0.9854	139.17	0.9865	193.49	0.9538	
0.14	150.93	0.9333	177.55	0.9874	157.10	0.9808	196.26	0.9318	
0.16	158.11	0.9592	185.18	0.9818	171.23	0.9854	199.60	0.9187	
0.18	167.91	0.9706	187.00	0.9905	205.51	0.9837	195.90	0.9218	
0.20	173.65	0.9795	180.06	0.9932	233.21	0.9781	195.48	0.9058	
0.22	178.35	0.9793	186.04	0.9847	231.63	0.9827	190.92	0.8940	
Mean	163.31		179.45		189.64		195.28		

Table 2. Decomposition activation energies of nanocomposites using Flynn-Wall-Ozawa method

Coats & Redfern (1964) method can be used to determine the most probable thermaldegradation mechanisms of poly(BOEMA)/organosilicate nanocomposites by following equation:

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

If the correct integral function $g(\alpha)$ is selected, a plot of $\ln[g(\alpha)/T^2]$ against 1000/T should give a straight line. Thus, the values of the apparent activation energy (E) for each heating rate in the conversion range can be determined. In order to determine the decomposition mechanisms of nanocomposites, it was compared with the activation energies obtained from Flynn-Wall and Ozawa method (Fraga & Nunez, 2001). Various $g(\alpha)$ kinetic models were analyzed according to Coats-Redfern (Coats & Redfern, 1964) method at 5, 10, 15 and 20 °C/min heating rates within the decomposition conversion range of 12% - 22%. Table 3 summarizes the calculated decomposition activation energies and linear regressions (*r*) for the probable kinetic

mechanisms of nanomaterials. Analysis of $g(\alpha)$ integral kinetic mechanisms showed that the apparent activation energy values of poly(BOEMA) homopolymer and its silicate nanocomposites followed the deceleration type mechanisms, which have the best agreement with the values obtained by Flynn-Wall and Ozawa method. The apparent activation energy of poly(BOEMA) homopolymer corresponding to R₃ mechanism was determined to be 163.39 kJ/mol at the heating rate of 15 °C/min. This value is very close to that of 163.31 kJ/mol obtained with Flynn-Wall and Ozawa method. From these results, it can be said that the mechanism of thermal degradation for poly(BOEMA) homopolymer between 12% and 22% conversion range probably followed a deceleration type phase boundary controlled reaction (R₃).

	Mechanism	5 °C/min		10 °C/min		15 °C/min		20 °C/min	
Polymer		E (kJ/mol)	r	E (kJ/mol)	r	E (kJ/mol)	r	E (kJ/mol)	r
Poly(BOEMA)	R_1	151.12	0.9908	135.96	0.9905	159.18	0.9954	165.20	0.9952
	R_2	154.16	0.9912	138.70	0.9909	162.37	0.9958	168.47	0.9952
	R_3	155.14	0.9914	139.58	0.9910	163.39	0.9959	169.52	0.9952
Poly(BOEMA)/ OVHAC:1%	D_1	199.41	0.9938	215.86	0.9956	193.44	0.9860	212.71	0.9934
	D_2	201.88	0.9939	218.53	0.9957	195.81	0.9857	215.37	0.9937
	D_3	204.40	0.9939	221.25	0.9958	198.22	0.9854	218.08	0.9941
	D_4	202.72	0.9939	219.44	0.9958	196.61	0.9856	216.27	0.9938
Poly(BOEMA)/ OVHAC:3%	\mathbf{D}_1	178.31	0.9973	212.68	0.9930	244.02	0.9896	176.90	0.9585
	D_2	180.55	0.9975	215.34	0.9933	247.04	0.9899	179.04	0.9578
	D_3	182.83	0.9977	218.04	0.9936	250.13	0.9901	181.21	0.9571
	D_4	181.31	0.9976	216.24	0.9934	248.07	0.9900	179.76	0.9576
Poly(BOEMA)/ OVHAC:5%	D_1	211.84	0.9811	218.76	0.9812	229.02	0.9746	213.48	0.9781
	D_2	214.52	0.9816	221.52	0.9818	231.92	0.9754	216.18	0.9788
	D_3	217.24	0.9822	224.33	0.9824	234.88	0.9761	218.94	0.9794
	D_4	215.42	0.9818	222.46	0.9820	232.91	0.9756	217.10	0.9790

 Table 3. Decomposition activation energies of nanocomposites for probable kinetic mechanisms using Coats-Redfern method

When the organosilicate was loaded at various amounts in poly(BOEMA) matrix, their solid-state degradation mechanisms also followed the general deceleration processes. But the decomposition kinetic mechanism of pure polymer shifted to dimensional diffusion type mechanisms (D_n) in the case of nanocomposites. Table 3 was re-analysed for determination of decomposition kinetic mechanisms of nanomaterials. For poly(BOEMA)/OVHAC:1% nanocomposite, the apparent activation energy value of 193.44 kJ/mol obtained at the heating rate of 15 °C/min corresponding to a deceleration type one-dimensional diffusion (D_1) mechanism was

in good agreement with the value obtained by the Ozawa method (179.45 kJ/mol). For poly(BOEMA)/OVHAC:3%, the best agreement with the apparent activation energy of Ozawa method was determined for D_n reactions. In particular, the apparent activation energy for D_3 three-dimensional diffusion process at a heating rate of 5 °C/min was calculated to be 182.83 kJ/mol. It was very close to the value of 189.64 kJ/mol determined for Ozawa method. Similar results were observed for the nanocomposite containing 5% organosilicate. It's probable thermodegradation kinetic mechanism was a deceleration type one-dimensional diffusion (D_1) mechanism, because the apparent activation energy determined for D_1 mechanism (211.84 kJ/mol at 5 °C/min) was in good agreement with the apparent activation energy using Ozawa method (195.28 kJ/mol).

4. Conclusions

X-ray diffraction analysis showed the silicate dispersion in the polymer matrix with an exfoliated structure. The thermal stabilities of nanocomposites were increased by loading organosilicate in the polymer matrix. It was observed that the decomposition temperature of nanocomposites containing 5 wt% organosilicate at 10% weight loss was approximately 14 °C higher than that of pure polymer. A positive correlation between the amount of added organosilicate phase and activation energies of nanocomposites was observed from the results of the thermal decomposition kinetic analysis. Introduction of the silicate phase in polymer enhanced the apparent activation energy from 163.31 kJ/mol to 195.28 kJ/mol using Flynn-Wall and Ozawa method within 12% - 22% decomposition conversion range. The mechanism of thermal degradation for pure polymer in this conversion range using Coats-Redfern method probably followed a deceleration type phase boundary controlled reaction (R₃), whereas in case of nanocomposites, it shifted to dimensional diffusion type (D_n).

5. Acknowledgements

We wish to thank the Adiyaman University Research Fund (ADYUBAP) for financially supporting this study (FEFYL2012-0006).

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Submitted : 13/05/2015 *Revised* : 04/11/2015 *Accepted* : 30/11/2015

خلاصة

تم تحضير المكون النانوى المتكون من عديد(2-(5-بروموبنزوفيوران-2-يل)-2-أوكسواينيل ميثاكريلات) واحادى الموريلوينيت المعدل عضويا بواسكة تقنية البلمرة فى نفس وعاء التفاعل. تم استخدام فينيل بنزيل ثنائى ميثيل هكساديسيل كلوريد الأمونيوم كعامل تعديل عضوى. أظهرت تقنية التحليل بحيود الأشعة السينية إنتشار السليكات فى مصفوفة البوليمر مع تركيب متقشر. إزداد الثبات الحرارى للمكونات النانوية مع إدخال السليكات العضوية إلى بنية البوليمر. كانت درجة حرارة التكسير للمكون النانوى المحتوى على 5% سليكات عضوية عندما كان الفقد الوزنى 10% فقط أعلى ب 14 درجة مئوية عن البوليمر النقى. تم تقييم التحليل الكيناتيكى لعملية تكسير المكون النانوى المحتوى على 5% سليكات فى مصفوفة إلى بنية البوليمر. وذلك فى مدى تكسير 21% - 22%. أدى إدخال السليكات فى البوليمر إلى تحسن طاقة التنشيط الظاهريه من 163.31 كيلوجول/ مول إلى 195.28 كيلوجول/ مول. من المحتمل أن ميكانيكية التكسير الحرارى للبوليمر النقى فى مدى التحول هذا يتبع نوعية تفاعل حدود الحالة التنشيط الظاهريه من 163.31 كيلوجول/ مول إلى 195.28 كيلوجول/ مول. من المحتمل أن ميكانيكية التكسير الحرارى للبوليمر النقى فى مدى التحول هذا يتبع نوعية تفاعل حدود الحالة التنشيط الظاهريه من 163.31 كيلوجول/ مول إلى 195.28 كيلوجول/ مول. من المحتمل أن ميكانيكية التكسير الحرارى للبوليمر النقى فى مدى التحول هذا يتبع نوعية تفاعل حدود الحالة ميكانيكية التكسير الحرارى للبوليمر النقى فى مدى التحول هذا يتبع.

الكلمات الرئيسة: طاقة التنشيط، البنزوفيوران، مكون البوليمر/ سليكات، ميكانيكية التفاعل، كيناتيكية التكسير الحراري.