Effect of modified bentonites on the crosslinking process of epoxy resin with alifphatic amine as curing agent

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Abstract: In this work the influence of modified bentonites on the process of epoxy crosslinking with triethylenetetramine (TETA) was investigated. Bentonites (BS) modified with quaternary phosphonium (QPS) and ammonium (QAS) salts were used as a nanofiller in the epoxy matrix (EP) in the amounts of 1 and 3 wt %. Gel time of the compositions was investigated using rotational rheometer at 30, 45 and 60 °C and activation energies of the compositions were determined. The storage G' and loss G'' moduli crossover criterion was used to determine the nanocomposites gel time variation. On the basis of the obtained results, it was found that the addition of modified aluminosilicates decreased the gel time of epoxy compositions at 30 and 45 °C, while at 60 °C it increased compared to unmodified epoxy resin. The obtained results indicate that the amount of modified aluminosilicate and the type of salt influence the reactivity of epoxy compositions. Among the tested systems, the most reactive was the composition of EP+3%BSQPS1, because the gel time at 30 °C and activation energy decreased by 1500 s and 8 J/mol, respectively, in relation to the unfilled EP resin. A more catalytic effect was observed in the case of bentonites modified with quaternary phosphonium salts, which may be associated with lower phosphorus electronegativity in relation to nitrogen and a lower viscosity of these systems.

Keywords: epoxy resin, modified bentonites, gel time, activation energy, rheometry.

Wpływ modyfikowanych bentonitów na proces sieciowania żywicy epoksydowej aminą alifatyczną

Streszczenie: Zbadano wpływ dodatku modyfikowanych bentonitów na proces sieciowania epoksydów za pomocą trietylenotetraaminy (TETA). Bentonit (BS) modyfikowany czwartorzędowymi solami fosfoniowymi (QPS) lub amoniowymi (QAS) użyto jako nanonapełniacz w osnowie epoksydowej (EP) w ilości 1 oraz 3 % mas. Za pomocą reometru rotacyjnego zbadano czas żelowania kompozycji w temp. 30, 45 i 60 °C, wyznaczono też ich energie aktywacji. Punkt żelowania wyznaczały przecinające się krzywe modułów zachowawczego G' i stratności G''. Na podstawie uzyskanych wyników stwierdzono, że dodatek do żywicy epoksydowej modyfikowanych glinokrzemianów spowodował skrócenie czasu żelowania kompozycji w temp. 30 i 45 °C, natomiast w temp. 60 °C nastąpiło jego wydłużenie w stosunku do czasu żelowania niemodyfikowanej żywicy epoksydowej. Uzyskane wyniki wskazują że zarówno ilość dodanego modyfikowanego glinokrzemianu, jak i rodzaj soli użytej do modyfikacji wpływają na reaktywność wytworzonych kompozycji epoksydowych. Spośród badanych układów największą reaktywność wykazywała kompozycja EP+3%BSQPS1; czas żelowania w 30 °C i energia aktywacji zmniejszyły się, odpowiednio, o 1500 s i 8 J/mol w stosunku do wartości odpowiadających nienapełnionej żywicy EP. Większy katalityczny efekt zaobserwowano w wypadku bentonitów modyfikowanych solami fosfoniowymi, co może wynikać z mniejszej elektroujemności fosforu niż azotu.

Słowa kluczowe: żywica epoksydowa, modyfikowane glinokrzemiany, czas żelowania, energia aktywacji, reometria.

Polymer-clay nanocomposites based on layered silicates (MMT) have been widely used in many branches of technology. The organoclays, due to their high aspect ratio and unique intercalation/exfoliation characteristics, are commonly used for improving, *e.g.*, mechanical [1], thermal [2] and barrier properties [3]. The wide application of these fillers in plastics processing results in the fact that rheological properties of nanocomposites

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are also an important area of research. In the processing of thermosetting composites it is important to monitor the gelation properties, in particular the curing time, viscosity increase and thermal effects of this process [4]. The most of these reports concentrated on the effect of the addition of bentonite modified with ammonium salts on the gelation properties of epoxy nanocomposites [5, 6]. Peila R. *et al.* [7] reported that the addition of nanoclay modified with quaternary ammonium salts increased viscosity and accelerated the curing process. They also observed, that the dispersion of nanoparticles in the epoxy matrix has a significant influence on the curing process. A smaller amount of the nanofiller dispersed better in the resin, thanks to which better results were achieved. Similar conclusions were obtained by Vijayan *et al.* [8], who examined the rheological properties of epoxy nanocomposites with modified clay I.28 E. The researchers observed, that nanocomposites cross-link more easily than unfilled resin, which is indicated by lower activation energy values. In turn, Penoff *et al.* [9] examined the curing behavior of epoxy nanocomposites obtained by incorporating clay modified with tributyl(hexadecyl)phosphonium bromide. They reported that this modifier was responsible for the reduction of the reaction yield of the epoxy-amine system. On the other hand, the application of higher amounts of MMT modified by poly(oxypropylene)diamine inhibits the curing reaction of epoxy resin, especially at the beginning of the process, due to the increase in viscosity and limited cation exchange reaction [10]. This effect was more visible in the case of nanocomposites containing MMT modified with high molecular weight diamine, which was characterized by prominent of interlayer spacing (4.6 nm). Generally, the curing kinetics of epoxy nanocomposites containing modified aluminosilicates depends on the amount of the additive, type of modifier and structure of the nanocomposite. However, there are no articles regarding the effect of the addition of layered aluminosilicates modified with quaternary phosphonium salts on the gelation time of epoxy compositions.

This paper is an extension of the research conducted so far in the Department of Polymeric Composites on obtaining compositions of epoxy resin with the addition of modified bentonite [11]. The aim of this work was to investigate the effect of bentonites modified with quaternary phosphonium and ammonium salts with different cation structure on the gelation properties of epoxy compositions. For this purpose, the gel times of epoxy compositions containing pristine bentonite, organobentonite and pristine salts, were determined using rheometry measurements. A rotational rheometer was equipped with a rotor oscillation function with a certain adjustable angle. In this type of experiment, the sample is subjected to sinusoidal alternating stress. Gel time studies can be used to kinetically describe the curing reaction by determining the activation energy.

EXPERIMENTAL PART

Materials

– Epoxy resin Epidian® 624 (EP) containing mostly diglycidyl ether of bisphenol A, and the curing agent triethylenetetramine (TETA) in a mass ratio 100 : 12, both commercial grade products of Ciech-Sarzyna Plant, Poland.

– Bentonite Specjal (BS) – technical product delivered by Zębiec S.A. Mining & Metal Plant in Zębiec near Starachowice (d_{hkl} = 12.5 Å).

– Quaternary ammonium salts (QAS) used as bentonite modifiers of the general formula $R_1R_2R_3R_4N^+Cl^-$, where R_1 and R_2 were -CH_3, R_3 was -$C_{12-14}H_{25-29}$ and R_4 was -$C_{12-14}H_{25-29}$ (QAS1) or -$CPhH_2$ (QAS2), produced by Lonza (Switzerland).

Quaternary phosphonium salts (QPS) used as bentonite modifiers of the general formula: $R_1R_2R_3R_4P^+Cl^-$, where R_1, R_2 and R_3 were -Ph, R_4 was -C_4H_9 (QPS1) or -$CPhH_2$ (QPS2), produced by Dishman Group (Holland).

Modification methodology

The procedure of modifying clays with quaternary ammonium or phosphonium salts with the use of a mixer with Parshall's built-in venturi had been previously developed and described in patent application [12]. It consists of introducing aqueous solution of quaternary salts to a suspension of a montmorillonite-rich bentonite in water, mixing using the agitator described in the utility model [13], removal of supernatant liquid, drying, grinding and sieving modified bentonite to obtain organophilized layered aluminosilicate of grain sizes below 60 μm.

Preparation of epoxy compositions

Compositions of epoxy resin containing 0.0, 1.0 or 3.0 wt % bentonite Specjal modified QAS or QPS have been prepared using four step homogenization procedure [11]. In order to prevent the mixture aging, it was kept at temp. approx. 4 °C.

Methods of testing

– The intergallery spacing (d_{001}) of clay, in EP compositions containing modified bentonites, was evaluated by wide-angle X-ray scattering (WAXS) using X-ray diffractometer type Nanostar with CuKα generator. The distance between clay platelets (d_{hkl}) was calculated from the Bragg formula and listed in Table 1.

– The gelation properties of the obtained compositions was tested using Discovery HR-2 rheometer, equipped with a temperature control system in the upper and lower part of the measuring system. The test was carried out in oscillatory mode using a 25 mm diameter aluminum parallel plates system rheometer using the following conditions: the width of the measuring gap – 1 mm, oscillation fre-

quency – 1 Hz, deformation – 0.2 %. The gel times were determined at three different temperatures: 23, 45 and 60 °C.

RESULTS AND DISCUSSION

As a result of gelation measurements, the following time-dependent curves were recorded: η* complex viscosity, G' storage modulus, which is a measure of elastic properties of the tested composition, and G'' loss modulus, which is a measure of viscous properties of the tested composition (Fig. 1). The gel point was the moment when G' and G' curves intersected and the tangent of mechanical loss angle tg δ reached the value of 1. According to the literature at the beginning of the curing process $G'' > G'$ because the material shows the properties of the liquid. As the crosslinking reaction progresses, both G' and G'' increase until both modules are cut and the epoxy compositions are crosslinked [14–16].

On the basis of the results presented in Table 1, it was found that the addition of modified bentonites decreased the curing time of epoxy compositions at 30 and 45 °C. Furthermore, the gel time decreased with organoclay loading. This is due to the presence of ammonium and phosphonium ions, which induce curing reactions between the aluminosilicate layers [17–19]. The shortest gel times were observed in compositions containing bentonite modified with quaternary phosphonium salts. Among these systems, EP+3%BSQPS1 was the fastest crosslinked, for which the gel time was 15 % shorter compared to the reference sample. In turn, among the compositions containing bentonite modified with ammonium salts, the sample EP+3%BSQAS1 was characterized
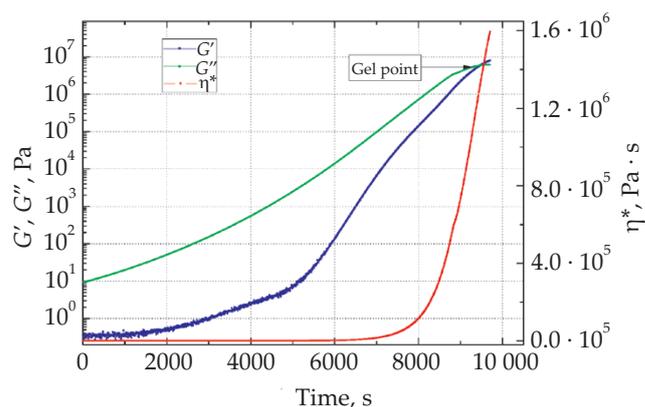

Fig. 1. Changes in storage (G') and loss (G'') moduli and complex viscosity (η*) during the crosslinking process of EP+1%BSQPS composition at 30 °C

by the shortest gel time in relation to unfilled resin, by about 1150 seconds. The more catalytic effect of bentonites modified with quaternary phosphonium salts can be related to lower phosphorus electronegativity in comparison to nitrogen. In the case of measurements carried out at 45 °C, the recorded differences in gel time were not so pronounced anymore. On the other hand, the gel times recorded for epoxy compositions at 60 °C were longer compared to the unmodified resin. The highest increase in gel time, by about 260 seconds, was observed in the composition containing 3 wt % of BSQAS2. Obtained results of gelation time recorded for compositions containing unmodified bentonite and selected QAS1 and QPS1 salts indicate that the type of salt used for modification

T a b l e 1. **Results of gelation properties of epoxy compositions containing modified aluminosilicates cured with triethylene-tetramine**

Type of composition	d_{hkl} Å	Initial viscosity Pa · s			Viscosity at the gel point · 10³, Pa · s			Gel time s			E_a kJ/mol
Temperature, °C		30	45	60	30	45	60	30	45	60	
EP6	–	1.154	0.368	0.190	905	491	98	9652	3975	1508	50.71
EP+1%BSQPS1	28.6	1.283	0.375	0.222	887	506	387	8765	3737	1700	43.69
EP+3%BSQPS1	27.1	1.650	0.463	0.166	856	398	400	8123	3532	1712	42.75
EP+1%BSQPS2	23.6	1.498	0.384	0.145	1330	465	409	9375	3626	1556	49.13
EP+3%BSQPS2	22.5	1.513	0.498	0.147	810	495	351	8916	3552	1530	48.22
EP+1%BSQAS1	38.4	2.225	0.487	0.239	1260	458	387	8847	3860	1542	47.85
EP+3%BSQAS1	38.0	2.736	0.853	0.574	926	349	421	8506	3428	1652	44.77
EP+1%BSQAS2	29.4	1.570	0.490	0.163	1210	483	389	9546	3654	1768	46.77
EP+3%BSQAS2	29.5	2.422	0.789	0.463	1087	521	453	9216	3584	1784	45.25
EP+1%BS	12.9	1.882	0.577	0.153	916	480	404	9954	3706	1557	50.77
EP+3%BS	12.8	2.114	0.869	0.210	900	463	398	10458	3987	1624	51.05
EP+1%QPS1	–	1.681	0.501	0.207	851	490	400	8756	3424	1686	45.13
EP+3%QPS1	–	1.872	0.551	0.237	927	500	365	8201	3158	1657	42.97
EP+1%QAS1	–	1.882	0.476	0.395	890	452	345	8371	3271	1775	43.66
EP+3%QAS1	–	1.996	0.508	0.358	880	470	412	8259	3304	1780	43.41

of bentonite is the factor influencing the changes in the studied parameter. The addition of unmodified bentonite resulted in a significant increase in gelation time, while the addition of only the salt significantly shortened it, in relation to EP. Furthermore, it was observed that the distance between layers of montmorillonite (d_{001}) is not the main factor influencing the curing process of epoxy compositions, which is opposite to the literature data [10].

The analysis of viscosity showed that the initial viscosity and viscosity in gel point increased compared to unfilled epoxy resin. The compositions modified with ammonium salts showed the highest initial viscosity, which limited the cation exchange reactions and, as a result, could lead to longer crosslinking in comparison to the compositions with BSQPS [20]. For composition with 1 wt % content of bentonite modified with QAS1 salt, the viscosity at 30 °C increased by 93 % compared to unfilled epoxy resin, whereas for 3 wt % content of this salt in the epoxy matrix an over 130 % increase in viscosity at 30 °C in relation to unfilled EP resin was observed. This may be due to a greater d-spacing (about 3.9 nm) of this modifiers, which indicates a better dispersion in the epoxy matrix, which may promote the formation of a strong thixotropic structure and, as a result, lead to an increase in initial viscosity. On the other hand, the compositions with lower reactivity were characterized by the highest viscosity value at the gel point.

The measurements were also used to determine the activation energy of the crosslinking reaction. It is assumed that the crosslinking energy includes only one reaction with a single activation energy value. Thus, the curing reaction rate can be expressed as a function of conversion and temperature [14]. For a given resin composition, the conversion rate at the gelation point has a constant value, therefore the gelation time equals the conversion time and can be related to the apparent kinetic constant of the reaction k' by the equation:

$$t_{gel} = c \cdot \frac{1}{k'} \qquad (1)$$

where: t_{gel} – gel time, c – constant.

According to Arrhenius equation, the apparent kinetic constant of the reaction k is related to the temperature as follows:

$$k = k_0'' \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \qquad (2)$$

where: E_a – apparent activation energy of the crosslinking response, k_0'' – pre-exponential factor of Arrhenius equation, R – gas constant, T – absolute temperature of cure.

As a results, the apparent activation energy E_a of cure reaction can be calculated from the gel time t_{gel}:

$$\ln t_{gel} = \frac{E_a}{R} \cdot \frac{1}{T} + C \qquad (3)$$

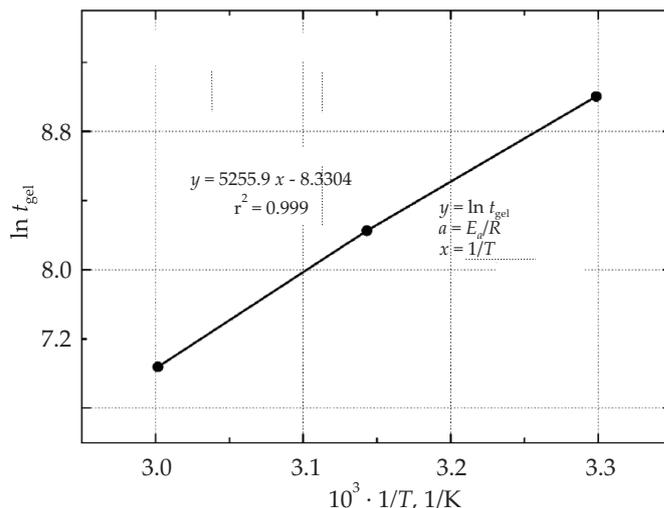Fig. 2. Arrhenius plot of EP+1%BSQPS1 composition

The above equation is a linear relationship between $\ln t_{gel}$ and the inverse of isothermal curing temperature. The apparent activation energy of the gelation process in the studied temperature range was calculated from the slope determined on the graph (Fig. 2) [14, 21].

It was found, that the addition of bentonite modified with QAS and QPS accelerated the crosslinking reactions of all compositions. The activation energy for the cure reaction of the EP resin was determined to be 50.71 kJ/mol. The lowest energy needed to initiate the crosslinking process was demonstrated by the EP+3%BSQPS1 composition, which E_a value was by 8.0 kJ/mol lower than E_a of the epoxy resin. Compositions containing bentonite modified with ammonium salts were also easier to be crosslinked, as E_a for these systems were lower by average 3.4 kJ/mol and 5.7 kJ/mol, for the 1 and 3 wt % BS loading, respectively, compared to EP resin. On the basis of the analysis of E_a value of EP composition containing unmodified BS and compositions containing selected salts QAS1 and QPS1 it was observed that the main influence on lowering the activation energy of the crosslinking process has a kind of quaternary salts used for modification of bentonite and a rapid increase of viscosity.

CONCLUSIONS

Compositions of epoxy resin with the addition of 1–3 wt % of bentonite modified with quaternary ammonium or phosphonium salts were obtained. The influence of the additive and type of salt used for modification of aluminosilicates on the reactivity of epoxy compositions was investigated. On the basis of the obtained results, it was found that the addition of bentonites modified with quaternary ammonium and phosphonium salts decreased the gel time of epoxy compositions. Higher reactivity of epoxy compositions containing modified aluminosilicates is also confirmed by the activation energy value, which decreased in relation to unmodified resin. This is due to the presence of alkylammonium and

alkylphosphonium ions, which induce curing reactions between layers of aluminosilicate [16]. A more catalytic effect was observed in the case of bentonites modified with quaternary phosphonium salts, which may be associated with lower phosphorus electronegativity in relation to nitrogen and a lower viscosity of these systems. Moreover, it was observed that the interplanar spacing (d_{001}) is a minor factor influencing the curing process of epoxy compositions.

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