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KOMPOZYTY
COMPOSITES

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INVESTIGATIONS OF CURING PROCESS FOR EPOXY-ISOCYANATE COMPOSITIONS

Epoxy-isocyanate compositions have been investigated. As components, epoxy resin Epidian 6, a product of the Chemical Works "Organika Sarzyna" in Nowa Sarzyna (Poland) and isophorone diisocyanate (IPDI) have been used. The compositions were prepared by mixing the epoxy resin with the diisocyanate in a molar ratio of epoxy group:isocyanate group 1:1 and 1:2. The accelerators were: the most often used - Girard's Reagent T (GR) as well as 1-ethylimidazole (1EI) and 1-butylimidazole (1BI). The catalyst was introduced in the amount of 0.5; 1.0 and 2.0 phr of epoxy resin. The curing process of the epoxy-isocyanate system was measured using a DSC Q-100 (TA Instruments) and an ARES Rheometer (Rheometrics Scientific). The glass transition value of the fully-hardened compositions were characterized in the second run of the DSC. The introduction of an imidazole derivate decrease of the maximum effect of the crosslinking process and the gel point of epoxy-isocyanate compositions. Increasing the accelerator content leads to an increase in the glass transition temperature of the obtained composites.

Keywords: epoxy resin, epoxy-isocyanate compositions, glass transition, curing process

BADANIE PROCESU SIECIOWANIA KOMPOZYCJI EPOKSYDOWO-IZOCYJANIANOWYCH

Badano kompozycje epoksydowo-izocyjanianowe, których główne składniki to żywica Epidian 6 oraz diizocyjanian izoforonu (IPDI). Żywicę epoksydową i izocyjanian mieszano w ilościach wagowych tak, aby na jedną grupę epoksydową przypadała jedna lub dwie grupy izocyjanianowe. Do kompozycji dodawano przyspieszacza w ilości 0,5; 1,0 i 2,0 cz.wag przypadających na 100 cz.wag żywicy epoksydowej; jako przyspieszaczy użyto opisywanego w literaturze odczynnika Girarda T (GR) oraz badanych 1-etyloimidazol (1EI) i 1-butyloimidazol (1BI). Wykorzystując metodę różnicowej mikrokalorymetrii skaningowej (DSC) oraz reometrię ARES, określono efekt energetyczny procesu sieciowania oraz temperaturę maksymalnego efektu egzotermicznego procesu sieciowania. W czasie drugiego przebiegu DSC oszacowano wartość temperatury zeszklenia usieciowanych kompozytów epoksydowo-izocyjanianowych. Wprowadzenie imidazoli spowodowało obniżenie temperatury maksymalnego efektu cieplnego procesu sieciowania oraz punktu żelowania kompozycji epoksydowo-izocyjanianowych. Zwiększenie zawartości przyspieszacza przyczynia się do podwyższenia temperatury zeszklenia otrzymanych kompozytów.

Słowa kluczowe: żywice epoksydowe, kompozyty epoksydowo-izocyjanianowe, temperatura zeszklenia, proces sieciowania

INTRODUCTION

High thermal resistant composites can be used in various applications, such as: automotive, electronics, aerospace and general industry. New materials - epoxy-isocyanate compositions with high thermal resistance that could be used in the electromechanical industry as material for tubular heaters have been investigated.

Epoxy and isocyanate compositions are known to react to form oxazolidones [1-6]: 2-oxazolidone and 4-oxazolidone derivatives, formed in a temperature range of 160÷250°C [7]. However, it is also known that substantial quantities of undesirable by-products are formed in a temperature range of 80÷120°C [7] in the following reactions: (i) trimerizations of isocyanate, (ii) reaction between epoxy resin and isocyanate to form aurethane bond (iii) formulation of biuret and allophanate compounds. As the reaction rate between the epoxy resin and isophorone diisocyanate without a catalyst at room temperature is low, to shift the reaction towards the desired products (containing an oxazolidone ring), a catalyst in the amount of 0.1 to 3.0 phr of epoxy resin was used [1-6].

The aim of the presented work was to investigate the influence of introducing a proper accelerator to epoxy-isocyanate compositions for the curing process and thermal resistance of the obtained composites.

MATERIALS AND METHODS

The compositions were prepared by mixing bisphenol A epoxy resin Epidian 6 (E6) from Organika Sarzyna S.A. in Nowa Sarzyna (Poland) with isophorone diisocyanate (IPDI) from Sigma-Aldrich and an appropriate catalyst: Girard's Reagent T (GR), 1-ethylimidazole (1EI) or 1-butylimidazole (1BI) from Sigma-Aldrich. The compositions were prepared by mixing the epoxy resin with the diisocyanate in a molar ratio of epoxy group:isocyanate group 1:1 and 1:2. The accelerators were: the most often used - Girard's Reagent T (GR) as well as 1-ethylimidazole (1EI) and 1-butylimidazole (1BI). The catalyst was introduced in the amount of 0.5; 1.0 and 2.0 phr of epoxy resin. The authors developed a new way to obtain epoxy-isocyanate compositions, which will be published as new patent application.

The curing process of the epoxy-isocyanate composition was characterized by using a differential scanning calorimeter DSC Q-100 by TA Instruments (USA), at a heating rate of 10°C/min in the temperature range of 0÷380°C and an ARES Rheometer (from Rheometrics Scientific) at a heating rate of 10°C/min in the temperature range of 30÷300°C, in 40 mm parallel-plate configuration with a gap of 1 mm. A glass transition value was determined during the DSC second run, at a heating rate of 10°C/min in the temperature range of 30÷300°C.

RESULTS

Selected DSC curves of epoxy-isocyanate compositions catalyzed with 1-ethylimidazole are presented in Figure 1.

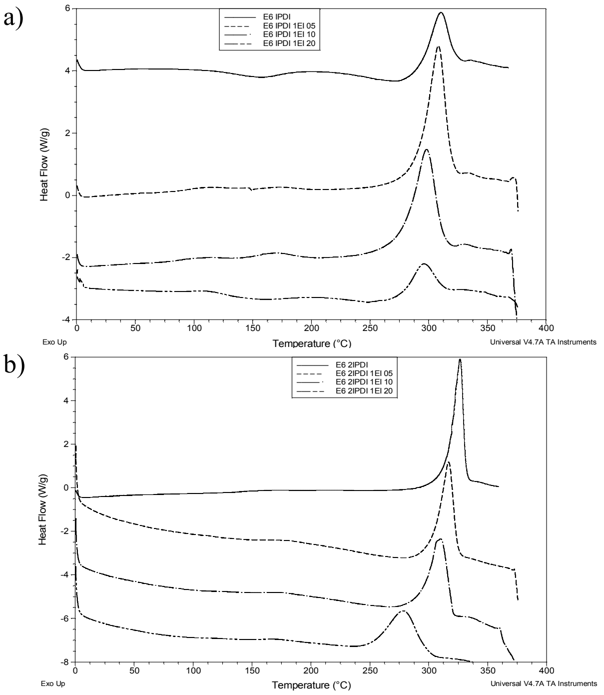

Fig. 1. DSC curves of epoxy-isocyanate compositions curing process (catalyzed with 1EI): a) molar ratio of epoxy group:NCO 1:1, b) molar ratio of epoxy group:NCO 1:2

Rys. 1. Krzywe DSC procesu sieciowania kompozycji epoksydowo-izocyjanianowych katalizowanych 1EI: a) udział molowy grupa epoksydowa:NCO 1:1, b) udział molowy grupa epoksydowa:NCO 1:2)

Two exothermic effects on the DSC curves might be observed: (i) in the range of 80 to 250°C (enthalpy below 40 J) assigned to the reaction between the epoxy group and the catalyst, and simultaneously the formulation of a urethane bond in the reaction between the secondary hydroxyl group and NCO as well as the trimerization of isocyanate; (ii) in a the range of 250 to 350°C assigned to the formulation of the oxazolidone ring.

From the DSC curves, both the characteristic maximum temperature (T_p) and the enthalpy of the curing process were determined. The thermal analysis results obtained for epoxy-isocyanate compositions with different catalyst content are presented in Figure 2.

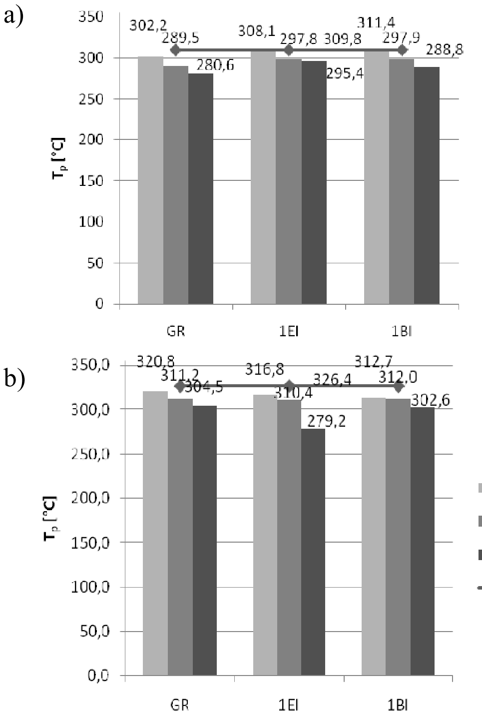

Fig. 2. Maximal temperature value for second peak of epoxy-isocyanate compositions curing process: a) molar ratio of epoxy group:NCO 1:1, b) molar ratio of epoxy group:NCO 1:2

Rys. 2. Wartość temperatury maksymalnej drugiego piku procesu sieciowania kompozycji epoksydowo-izocyjanianowych: a) udział molowy grupa epoksydowa:NCO 1:1, b) udział molowy grupa epoksydowa:NCO 1:2

The presence of a catalyst accelerated the epoxy resin/diisocyanate compositions curing process, particularly when the highest amount was used. The curing process of the epoxy:isocyanate mixture occurred slightly faster for the compositions with the molar ratio of epoxy:NCO group 1:1 than 1:2.

The maximal temperature values are similar for epoxy-isocyanate compositions independent of the diisocyanate amount and are smaller than the composition without a catalyst (E6/IPDI or E6/2IPDI). The lowest values of this parameter were exhibited by the composition with the highest 1-ethylimidazole content (2.0 phr) with the molar ratio of epoxy:isocyanate group equal to 1:2.

The enthalpy values of the epoxy-isocyanate compositions curing process are generally higher when a catalyst was used, particularly when 1-ethylimidazole was applied (Fig. 3a). Similar tendencies can be observed in the case of the compositions containing a higher amount of isophorone diisocyanate where the exothermic effects are smaller than for the materials without a catalyst (Fig. 3b) for the composition of the molar ratio epoxy:isocyanate group equal to 1:1 (Fig. 3a). The compositions with the lowest content of accelerators: Girard's Reagent T and 1-butylimidazole, exhibited a smaller exothermic effect of the curing process when compared to the material without an accelerator (Fig. 3b).

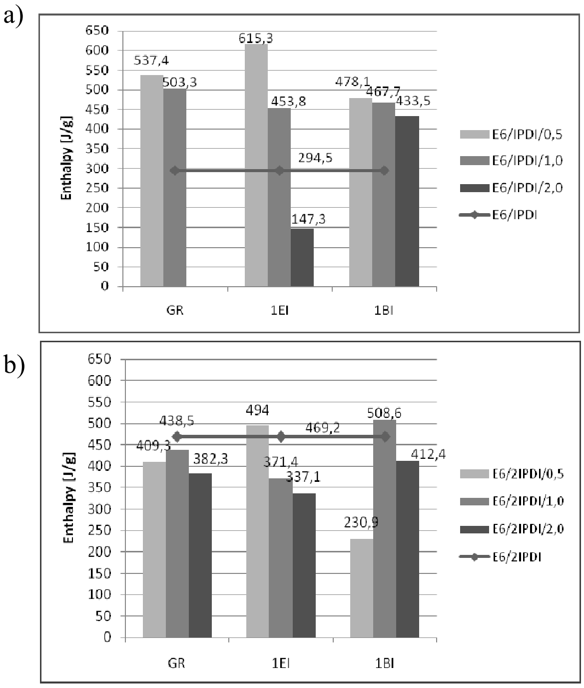

Fig. 3. Enthalpy values for second peak of epoxy-isocyanate compositions curing process: a) molar ratio of epoxy:NCO group 1:1, b) molar ratio of epoxy:NCO group 1:2)

Rys. 3. Entalpia drugiego piku procesu sieciowania kompozycji epoksydowo-izocyjanianowych: a) udział molowy grupa epoksydowa:NCO 1:1, b) udział molowy grupa epoksydowa:NCO 1:2

Figure 4 shows the ARES rheometric curves (viscosity vs temperature) of the epoxy-isocyanate compositions curing process with different contents of 1-ethylimidazole.

The epoxy-isocyanate composition curing process might be described by the viscosity changes (Fig. 4), storage as well as loss modulus versus temperature; from the intersection of the storage and loss modulus, the gel point could be determined.

Independent of the kind of epoxy-isocyanate composites, the rheometric curves could be divided into several ranges: (i) from 40 to 120°C where slight viscosity changes might be observed, (ii) from 120 to 200÷250°C with decreasing viscosity caused by minor reactions (similar to the DSC curves) and (iii) above 200÷250°C with a high viscosity increase assigned to the major reaction (the initial temperature of this range is related to the amount of the catalyst). Independent of the isocyanate content, the highest viscosity changes might be observed for the epoxy-isosyanate composition with the highest amount of 1-ethylimidazole. The lowest viscosity increase is noticed for the composition without an accelerator with the epoxy:isocyanate group molar ratio equal to 1:1.

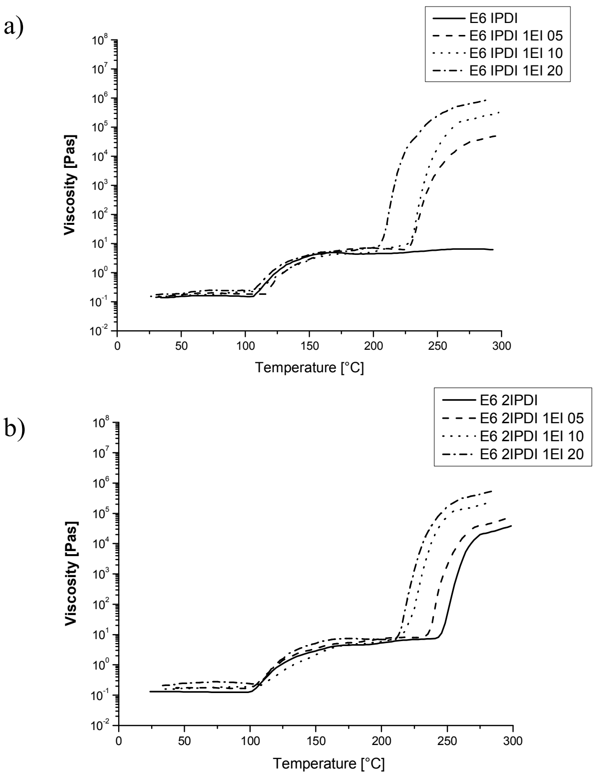

Fig. 4. Rheometric curves of epoxy-isocyanate compositions curing process (catalyzed with 1EI): a) molar ratio of epoxy group:NCO 1:1, b) molar ratio of epoxy group:NCO 1:2

Rys. 4. Krzywe reometryczne procesu sieciowania kompozycji epoksydowo-izocyjanianowych katalizowanych 1EI: a) udział molowy grupa epoksydowa:NCO 1:1, b) udział molowy grupa epoksydowa:NCO 1:2

Figure 5 shows the gel point values of the epoxy-isocyanate compositions.

The gel point values for the compositions without a catalyst are slightly higher than for the compositions with accelerators, particularly in the case of the mixture with the molar ratio of epoxy:NCO group 1:1 (300°C). The gel point value of the epoxy-isocyanate material with the molar ratio 1:2 E6/2IPDI (247°C) is much lower than for 1:1 E6/IPDI (300°C). The highest amount of catalysts used causes the temperature of the gel point to decrease in comparison to the lowest content to about 20°C for the composition with the molar ratio 1:1 and from 20°C (with 1-butylimidazole as the catalyst) to 40°C (with Girard's Reagent T as the accelerator) in the case of the mixture with highest diisocyanate content. The gel point values demonstrated a similar tendency like the temperature of the maximum of the exothermic process (Fig. 2a and 2b), but they are generally smaller by 60°C in the case of the composition with a lower isophorone diisocyanate content and by 80°C for materials with the molar ratio of epoxy:NCO group 1:2.

Figure 6 presents the glass transition of epoxy-isocyanate composites.

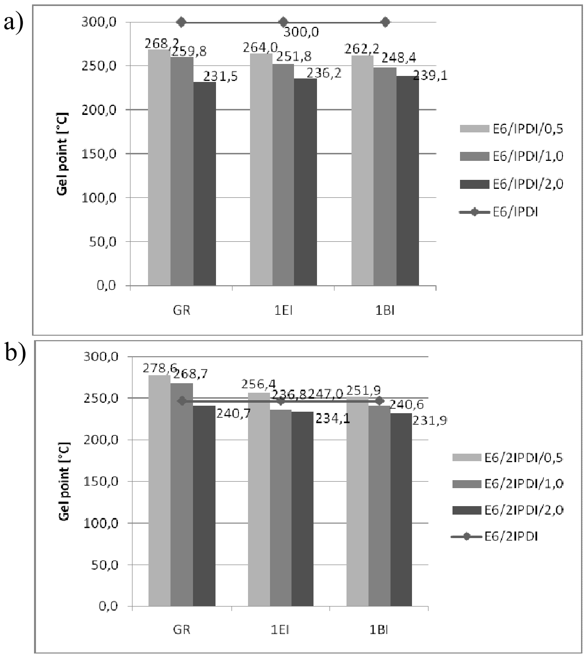

Fig. 5. Gel point values of epoxy-isocyanate compositions with different catalyst: a) molar ratio of epoxy group:NCO, 1:1, b) molar ratio of epoxy group:NCO 1:2

Rys. 5. Punkt żelowania kompozycji epoksydowo-izocyjanianowych z różnymi katalizatorami: a) udział molowy grupa epoksydowa:NCO 1:1, b) udział molowy grupa epoksydowa:NCO 1:2

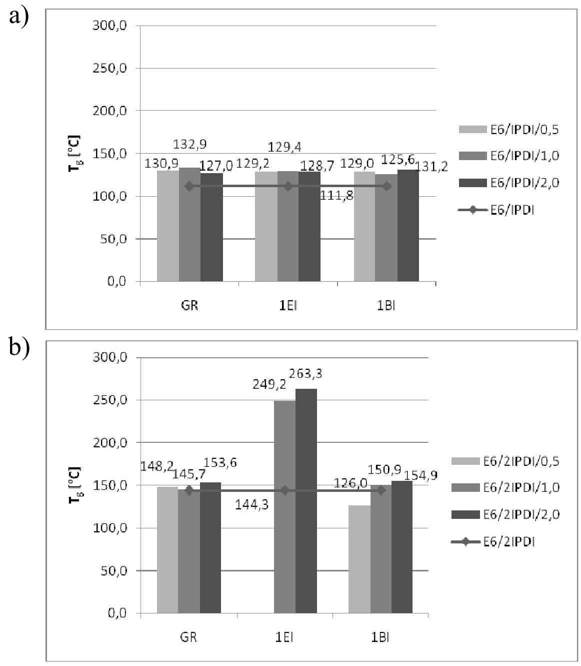

Fig. 6. Glass transition of epoxy-isocyanate composites cured using different catalyst: a) molar ratio of epoxy group:NCO 1:1, b) molar ratio of epoxy group:NCO 1:2

Rys. 6. Temperatura zeszklenia kompozytów epoksydowo-izocyjanianowych sieciowanych przy użyciu różnych katalizatorów: a) udział molowy grupa epoksydowa:NCO 1:1, b) udział molowy grupa epoksydowa:NCO 1:2

The glass transition of epoxy-isocyanate composites are in the ranges of: (i) from 112°C for the composite hardened without any accelerator, to about 133°C for the epoxy-isocyanate material cured with Girard's Reagent T (Fig. 6a) and (ii) from 126°C for the epoxy-isocyanate composite accelerated with the lowest content of 1-butylimidazole to 155°C, cured by introducing the highest catalyst amount (except the composites hardened with 1-ethylimidazole, whose glass transition temperatures are higher than 245°C (the obtained values can be a result of the difficulty of interpreting specific heat changes caused by a high degree of crosslinking)). Epoxy-isocyanate composites with a higher isophorone diisocyanate content have higher glass transition values than materials with a lower epoxy:NCO factor.

CONCLUSION

Introducing catalysts to epoxy-isocyanate material accelerates its curing process independent of the isocyanate content. The effect of using 1-imidazole derivatives, such as: 1-ethylimidazole and 1-butylimidazole is similar to that described in the references for Girard's Reagent T, although no significant reduction of curing process enthalpy was noticed in the case of toluene diisocyanate (TDI), might be observed. The great advantage of using 1-imidazole derivatives is their excellent solubility in epoxy resin. Although isophorone diisocyanate is less active than toluene diisocyanate, by using it, higher glass transition temperature values (thermal stability) were obtained.

In order to evaluate the effect of using imidazole derivatives on thermal resistance as well as glass transition temperature, the authors plan to further research these materials.

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