MAGDALENA URBANIAK*), KAROL GRUDZIŃSKI

Szczecin University of Technology
Department of Mechanics and Machine Elements
Al. Piastów 19, 70-310 Szczecin, Poland

Conversion-Temperature-Transformation (CTT) cure diagram for EPY® epoxy system

Summary — Thermal decomposition of the filled epoxy system EPY® ("Epidian 6" with triethylenetetramine), applied for the production of machine foundation chocks, was studied using thermogravimetry and differential thermal analysis (TG-DTA). The results obtained and the results previously reached by differential scanning calorimetry (DSC) and rotational viscometry as well as by empirical model of the dependence of glass transition temperature on conversion degree let determine the cure diagram conversion — temperature — transformation (CTT) for the system studied. The cure diagram obtained makes possible the general insight into thermo-mechanical behavior of EPY® system during its curing and this way can be the useful tool for the assessment of curing quality of the material, required especially in the use for foundation chocks in their various applications.
Key words: epoxy system, thermal decomposition, curing, gelation, conversion, glass transition temperature, CTT diagram.

DIAGRAM SIECIOWANIA KONWERSJA-TEMPERATURA-PRZEMIANA (CTT) UKŁADU EPOKSYDOWEGO EPY®

Streszczenie — Metodą termograwimetrii i różnicowej analizy termicznej (TG-DTA) badano rozkład termiczny napełnionego układu epoksydowego EPY® (Epidian 6 z trietylenotetraaminą) stosowanego do produkcji podkładek fundamentowych maszyn (tabela 1, rys. 3). Wyniki tych badań razem z uzyskanymi wcześniej za pomocą skaningowej kalorymetrii różnicowej (DSC), wiskozymetrii rotacyjnej oraz zastosowanie modelu empirycznego zależności między temperaturą zeszklenia a stopniem konwersji pozwoliły na wyznaczenie diagramu sieciowania konwersja-temperatura-przemiana (CTT) tego układu (rys. 1 i 2). Otrzymany diagram sieciowania (rys. 4) umożliwia ogólny wgląd w termomechaniczne zachowanie się tworzywa EPY® podczas jego utwardzania i może być użytecznym narzędziem do oceny jakości utwardzania tego materiału, jakości wymaganej zwłaszcza przy produkcji podkładek fundamentowych do różnych zastosowań.
Słowa kluczowe: układ epoksydowy, rozkład termiczny, sieciowanie, żelowanie, konwersja, temperatura zeszklenia, diagram CTT.

The properties of the final material are intimately related to gelation and vitrification, so the information about these two phenomena is required to characterize an epoxy resin system and to specify an efficient curing program to ensure that the properties of the thermoset are optimized for a specific application [1, 2]. A useful tool for the curing state analyzing of the thermoset is the conversion-temperature-transformation (CTT) cure diagram introduced by Addabo and Williams [3]. A schematic CTT diagram is shown in Figure 1, where the relationship between the chemical conversion in the thermosetting polymer and the glass transition temperature developed and phenomenological changes that took place during the curing [3—6] are presented. This diagram is grounded in gelation line (α_{gel}), vitrification curve [$\alpha = f(T_g)$] and initial temperature thermal degradation line (T_{di}) and also three characteristic thermoset temperatures: T_{g0}, $_{gel}T_g$ and $T_{g\infty}$. T_{g0} is the temperature below of that no significant reaction of the epoxy-hardener mixture occurs. $_{gel}T_g$ is the temperature at which gelation and vitrification can simultaneously occur in an ideal system. $T_{g\infty}$ is the glass transition temperature of the fully reacted material. These contours show different states in which a thermosetting material may be found in the curing process, *i.e.*: liquid, rubber ungelled glass, gelled glass, and degradation states.

The diagram shows clearly that the cure always starts at $T > T_{g0}$. The gelation line shows the transition from a liquid to a rubber or, eventually, from an ungelled glass to a gelled glass. One can see that at a particular temperature $_{gel}T_g$, the liquid is directly transformed into a

*) To whom all correspondence should be addressed; e-mail: Magdalena.Urbaniak@ps.pl

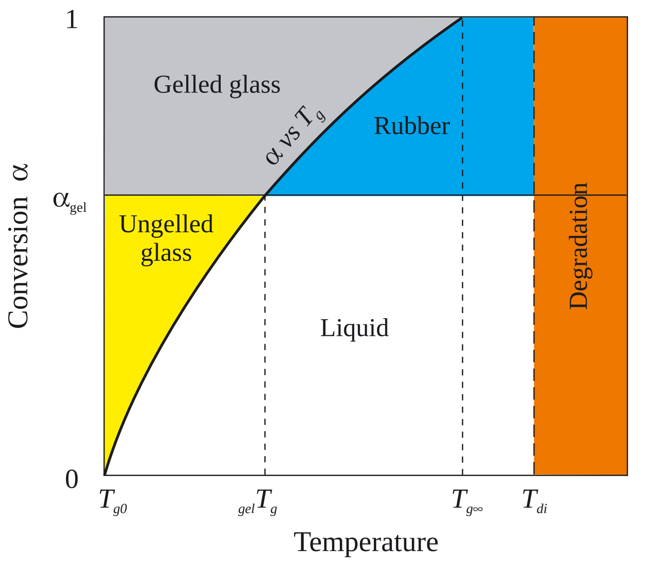

Fig. 1. Generalized conversion-temperature-transformation (CTT) cure diagram for a thermosetting system, showing four critical temperatures (T_{g0}, ${}_{gel}T_g$, $T_{g\infty}$ and T_{di}), various states of the material, and its gelation, vitrification and degradation contours

gelled glass upon gelation. At the left of the vitrification curve, either ungelled or gelled glass is obtained.

A CTT cure diagram is based on the data similar to the data collected for the time-temperature-transformation (TTT) isothermal cure diagram introduced and developed by Gillham *et al.* [7, 8]. The TTT diagram calculated for the EPY® epoxy system was presented in the previous article [9]. CTT diagram can be developed through a certain transformation of TTT diagram [9, 10] bearing in mind that gelation occurs at the same chemical conversion regardless of temperature [5]. Therefore, a gelation curve in TTT diagram becomes transformed into a gelation line in CTT diagram, whereas the vitrification curve is now presented as the glass transition conversion-temperature curve (Fig. 1).

The EPY® epoxy system — the object of the investigations presented in this and earlier paper [9] is applied as a material to foundation chocks in seating of a ship machinery and installations and also for many various heavy land-based machines in mining, power industry and other fields of heavy industry and building engineering [11].

The purpose of the studies presented in this article was to demonstrate the possibilities of developing a conversion-temperature-transformation (CTT) diagram for the EPY® epoxy system by means of empirical and theoretical ways without running costly and time consuming experimental measurements [10]. The CTT diagram developed in this way can give widespread insight into the thermo-mechanical behavior of the EPY® epoxy system during curing process and it let obtain information on its curing degree that determines the thermo-mechanical properties of the material.

EXPERIMENTAL

Materials

The main components of the investigated material, whose trade name is EPY® (from Marine Service Jaroszewicz), are: epoxy resin Epidian 6 (epoxy number 0.532 mole/100 g) and a curing agent Z-1 (triethylenetetramine) both produced by Chemical Works Organika-Sarzyna in Nowa Sarzyna. The resin and curing agent ratio is constant and equals 14 parts of the curing agent per 100 parts of the resin. The epoxy system is completed with additives bestowing appropriate technological and useful properties upon the material. The chemical structures of the reacting materials are shown in the previous article [12].

Method of testing

The thermal degradation of the epoxy system was examined by thermogravimetry-differential thermal analysis method using thermal analyzer, Setaram TG-DTA 92-16. The "as-mixed" sample of the system components (prepared just before measurements), 20 mg in weight, located in corundum pot was heated in the temperature range from 15 to 800 °C under nitrogen atmosphere at the of 10 °C/min.

DEVELOPMENT OF CTT DIAGRAM

An experimental development of CTT diagram for thermoset resin carried out only on the basis of experimental results involves costly and time consuming experimental measurements. It was shown in the previous article [9] that the number of necessary experimental

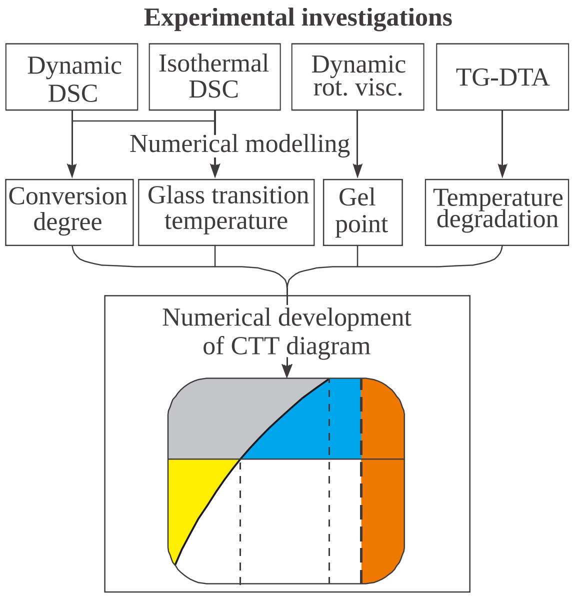

Fig. 2. Flow chart of the experimental and numerical development of CTT diagram

measurements can be limited to a minimum thanks to the implementation of numerical modelling. The empirical models were derived from the experimental results obtained using dynamic and isothermal differential scanning calorimetry (DSC) and rotation viscometry (ARES) (both published previously [9]) together with new thermogravimetry (TG-DTA) results in order to predict the progression in the degree of curing (especially at the gel point), and the glass transition temperature. The models appropriately combined allowed to develop a numerical representation of CTT diagram that is shown schematically in Figure 2.

RESULTS AND DISCUSSION

Thermal degradation results

Thermogravimetric curve (TG) and differential thermogravimetric curve (DTG) of the uncured resin-hardener mixture shown in Figure 3 illustrate the weight loss and thermal decomposition rate of the EPY® epoxy system as a function of temperature. The measurement results of thermal stability are collected in Table 1. The EPY® epoxy system has a good thermal resistance since the onset temperature for decomposition (T_{di}) is 258 °C (weight loss of 1 %) while considerable decomposition begins above 300 °C and ends (T_{df}) at 536 °C where the essential weight loss is 94 %. The minimum of thermal decomposition rate for the EPY® system obtained from DTG curve is found at 361 °C (Fig. 3).

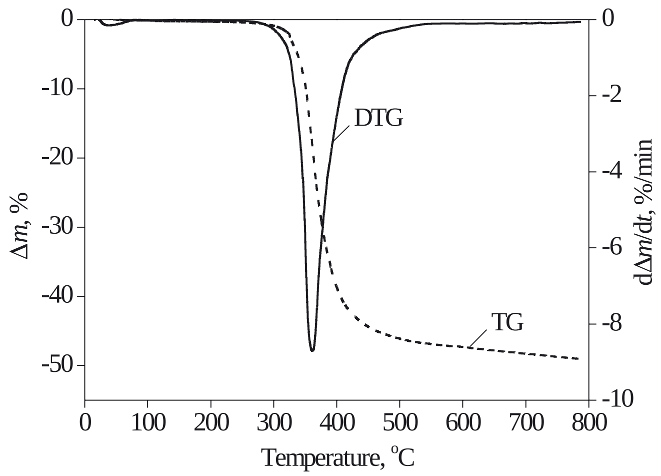

Fig. 3. Weight loss (Δm) and time derivative of Δm (dΔm/dt) curves for thermal degradation of EPY® epoxy system at heating rate 10 °C/min

CTT diagram

CTT diagram of curing for the EPY® epoxy system is given in Figure 4. To plot CTT diagram it is necessary to know three characteristic temperatures: the initial glass transition temperature of the system (T_{g0}), the temperature at which gelation and vitrification occur simultaneously ($_{gel}T_g$) and the glass transition temperature of the fully cured system ($T_{g\infty}$). For the system studied here T_{g0} = -45.6 °C and $T_{g\infty}$ = 111.2 °C were determined experimentally by means of DSC and $_{gel}T_g$ was calculated using DiBenedetto's equation and the value of the conversion degree at gelation α_{gel} = 0.58 was determined experimentally using ARES and DSC methods [9].

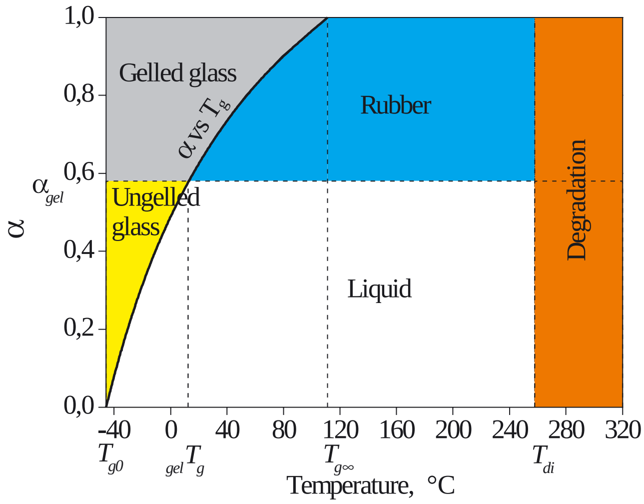

Fig. 4. Calculated CTT cure diagram for the EPY® material

The main contour in CTT diagram constitutes the vitrification curve (α *vs.* T_g) that was determined using DiBenedetto's equation. A good fit of the experimental data with DiBenedetto's equation was obtained which was shown in the previous article [9].

The line of the conversion degree at gelation α_{gel} = 0.58 in CTT diagram was also previously determined experimentally using ARES and DSC methods [9]. This line intersects the vitrification curve at the point related to $_{gel}T_g$ = 12.5 °C in CTT diagram.

Table 1. Results of TG-DTA investigation of thermal degradation of the epoxy system

T_{di}[a)], °C	T_{dmin}[b)], °C	T_{df}[c)], °C	Weight loss at different temperatures, %						
			250 °C	300 °C	350 °C	400 °C	450 °C	500 °C	550 °C
258	361	536	0.92	2.69	30.98	71.43	88.01	92.01	93.73

[a)] T_{di} — initial temperature of thermal degradation. [b)] T_{dmin} — temperature of minimum degradation rate. [c)] T_{df} — final temperature of thermal degradation.

The temperature line T_{di} = 258 °C relating to the onset temperature of thermal degradation was determined experimentally in this study using TG-DTA method.

The curves and lines in CTT diagram (Fig. 4) delineated in this way segregate the following states: liquid, rubber, ungelled glass, gelled glass and degradation which epoxy system can go through under given cure conditions.

CTT diagram shows that during curing of the studied system, its glass transition temperature T_g increases in a nonlinear way from the initial value of T_{g0} =-45.6 °C (at the conversion degree α = 0) through that to gelation, *i.e.* ${}_{gel}T_g$ = 12.5 °C (α = 0.58) to the final value of $T_{g\infty}$ = 111.2 °C (at maximum conversion) due to the growth in the network crosslinking density. The relation between glass transition temperature and conversion depicted by the vitrification curve let use T_g value as a direct measure of the conversion degree that in practice can be assumed as determining the thermo-mechanical properties of the material. CTT diagram shows also that curing of the material at too high temperature ($T_c >> T_{g\infty}$ = 111.2 °C) can lead to a thermal degradation which starts at T_{di} = 258 °C resulting in a loss of useful material properties.

CONCLUSIONS

The conversion-temperature-transformation (CTT) cure diagram for the EPY® epoxy system developed by means of empirical and theoretical ways can be a useful tool for assessing of curing process quality of this material. This diagram depict the most essential physical parameters of the epoxy resin (T_{g0}, ${}_{gel}T_g$, $T_{g\infty}$ and T_{di}). Different states of the studied system in which it may be found during the curing process are shown as functions of temperature and conversion degree. The diagram also points out the thermal degradation region. The data obtained from the vitrification curve in CTT diagram let get information on the curing degree of the system and allow to determine the final mechanical and thermal properties of the material.

CTT diagram is a valuable complement to TTT isothermal cure diagram (time-temperature-transformation) described previously [9, 10] for the EPY® epoxy material and both of them are useful tools to choose an optimal path of this material curing. CTT diagram makes possible to choose a cure degree that would secure obtaining the most appropriate and useful properties needed for a specific application of the material.

REFERENCES

1. Barral L., Cano J., López A. J., López J., Nogueira P., Ramírez C.: *J. Appl. Polym. Sci.* 1996, **61**, 1553.
2. Simon S. L., Gillham J. K.: *J. Appl. Polym. Sci.* 1994, **53**, 709.
3. Adabbo H. E., Williams R. J.: *J. Appl. Polym. Sci.* 1982, **27**, 1327.
4. Pascault J.-P., Sautereau H., Verdu J., Williams R. J. J.: "Thermosetting Polymers", Marcel Dekker, New York 2002, pp. 119—145.
5. Bryant E., Chartoff R.: "Crosslink Density and the Glass Transition in Thermosetting Polymers" in http://www.udri.udayton.edu/rpdl/Paper_CROSDENS/paper, University of Dayton 1998.
6. Williams R. J. J.: "Curing of Thermosets" in "Developments in Plastics Technology" (Ed. Whelan A., Craft J. L.), Elsevier Applied Science, London 1985, vol. 2, pp. 339—379.
7. Gillham J. K., Benci J. A., Noshay A.: *J. Appl. Polym. Sci.* 1974, **18**, 951.
8. Gillham J. K.: *Polym. Eng. Sci.* 1979, **19**, 676.
9. Urbaniak M., Grudziński K.: *Polimery* 2007, **52**, 50.
10. Urbaniak M.: "Badania procesu utwardzania i jego wpływu na właściwości mechaniczne tworzywa epoksydowego EPY stosowanego na podkładki fundamentowe maszyn", PhD thesis, Szczecin University of Technology, Department of Mechanics, Szczecin 2004.
11. Grudziński K., Jaroszewicz W.: "Seating of machines and devices on foundation chocks cast of EPY resin compound", ZAPOL, Szczecin 2004, pp. 19—32.
12. Urbaniak M., Grudziński K.: *Polimery* 2004, **49**, 89.

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