*Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 13-18*

# THERMAL CHARACTERIZATION OF POLYURETHANE ACRYLATE RESINS

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(Received 9 September, 1998)

## Abstract

Polyurethane acrylate resins cured by two different ways, a thermal way and a photochemical way, are investigated by means of differential scanning calorimetry (DSC) and thermally stimulated depolarization currents (TSDC). Even if both curing methods lead to the same material from a chemical point of view, we show that important differences exist between the thermocured resin and the photocured resin in terms of molecular relaxation behaviour.

**Keywords:** DSC, enthalpic relaxation, polyurethane, TSDC

## Introduction

Polyurethanes and especially polyurethane acrylate resins are of prime interest because different methods of curing can be performed to obtain the final solid product. Moreover, a large variety of systems can be achieved by changing the type of isocyanate groups or the length of aliphatic chains between isocyanate groups, in such a way that the molecular relaxations below the glass transition are expected to scan a large relaxation time range. The molecular relaxation can be investigated by means of calorimetry and thermally stimulated depolarization currents [1, 2]. The complex spectrum obtained by TSDC technique allows the determination of a polarization value which depends on the number of relaxing dipoles. For DSC investigations, the molecular relaxation below the glass transition can be described from the relaxation time $\tau$ given by the Tool-Narayanaswamy-Moynihan relationship [3]:

$$\tau = \tau_0 \exp\frac{x\Delta h^*}{RT} \exp\frac{(1-x)\Delta h^*}{RT_\mathrm{f}} \tag{1}$$

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*1418–2874/99/ $ 5.00*

*Akadémiai Kiadó, Budapest*
*Kluwer Academic Publishers, Dordrecht*

where $x$ is the non-linearity parameter ($0 \leq x \leq 1$), $\Delta h^*$ the apparent activation energy and $T_f$ the fictive temperature defined by Tool [4] (defined as the intercept between the vitreous state enthalpic line and the liquid state enthalpic line). The apparent activation energy depends on the number of relaxing units and on the configurational entropy of the system [5]:

$$\Delta h^* = \frac{s_c^* \Delta\mu}{S_c} \tag{2}$$

$$\text{with } S_c = \frac{s_c^*}{z^* N_a} \tag{3}$$

where $\Delta\mu$ is the elementary excitation energy per particle, $S_c$ the macroscopic configurational entropy, $s_c^*$ the configurational entropy of the smallest number of particles capable of rearranging, $N_a$ the Avogadro's number and $z^*$ the minimum value of the number of particles that cooperatively rearrange.

According to Moynihan *et al.* [6], this activation energy can be estimated from the variations of $T_f$ with the cooling rate:

$$\frac{\mathrm{d}\ln(q^-)}{\mathrm{d}\frac{1}{T_f}} = \frac{-\Delta h^*}{R} \tag{4}$$

In this work, we present the first results concerning the values of $\Delta h^*$ and $P$ obtained for resins cured by a thermal way and by a photochemical way.

## Materials and methods

Polyurethane acrylate resins are synthesized from a prepolymer based on hexamethylene diisocyanate (HDT) and hydroxy-2-ethyl methacrylate. The synthesis of the prepolymer has been described elsewhere [7]. Two different ways for the curing process are used to obtain polyurethane acrylate networks, a classical thermal way and a photochemical way. The thermocuring of this resin consists in curing the prepolymer with peroxide at 115°C during 24 h. The photocuring has been considered, without diluent reactive material, in the presence of the photoinitiator 2,2-dimethyl-2-hydroxyacetophenone, dissolved in the oligomer by stirring at room temperature. The radical photopolymerization of the resin was followed using a Perkin Elmer DSC-7 calorimeter topped by an irradiation unit (100 W Hg lamp) with two quartz windows. More details about these experiments and characterization of the resulting crosslinked resin are given in [7] where it was shown that the cure reaction has reached its maximum. The present calorimetric investigations are performed with a Perkin Elmer system 7 differential scanning calorimeter. Temperature scans were carried out on 20 mg samples at a heating rate of 20 K $\mathrm{min}^{-1}$ under a nitrogen atmosphere. Temperature calibrations are made using indium and zinc standards. The changes in specific heat capacity at the glass transition temperature are determined using the specific heat capacity of sapphire as standard. The apparent activation energy, $\Delta h^*$ is determined from the variations of the fictive thermodynamic equilibrium temperature with the cooling rate. Here, the procedure is to cool the sample in the DSC at a cooling rate in the range from 100 to 0.5 K min$^{-1}$, from a temperature $T_2$=180°C above $T_g$ down to a temperature $T_1$=40°C well below $T_g$. Then the sample is heated without any annealing time up to $T_2$ with the same heating rate of 20 K min$^{-1}$. The fictive temperature was calculated from the heating scan in these cycles using the method proposed by Moynihan [6].

Thermally stimulated depolarization current (TSDC) measurements were performed with an apparatus developed in our laboratory [8]. Samples are about 1 mm thick and the electrodes have a diameter of 8 mm. The samples are first heated to a polarization temperature $T_p$=150°C above the glass transition temperature $T_g$. Then, they are submitted to an electric field of 450 kV m$^{-1}$ for a period of 2 min at $T_p$. This allows the orientation of dipoles with relaxation times smaller than the period of polarization. Then the polarization is frozen in by decreasing the temperature at a constant cooling rate of 10 K min$^{-1}$, the electric field is cut off, a short circuit is set up and the temperature is increased with a constant rate of 10 K min$^{-1}$, allowing the gradual relaxation of different polar units and the measurement of the depolarization current.

## Results and discussion

Figure 1 shows the calorimetric curves obtained on each sample. By crossing the glass transition temperature range, we only observe a change in the specific heat capacity. The values of the glass transition temperature are exactly the same for both samples (Table 1). No exotherm related to further curing is observed at higher temperature indicating that the degree of cure has reached its maximum.

Figure 2 represents the TSDC complex spectra obtained on each sample. At low temperature, we observe for both systems that the same peaks appear at the same temperatures, respectively –120 and –20°C, and with the same magnitudes. These

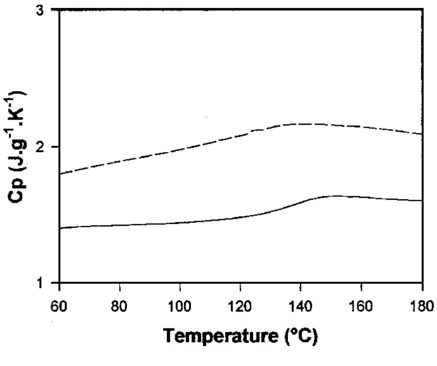

**Fig. 1** DSC heating curves obtained with a heating rate of 20 K min$^{-1}$ on the thermocured resin (dashed line) and on the photocured resin (full line), without any annealing time

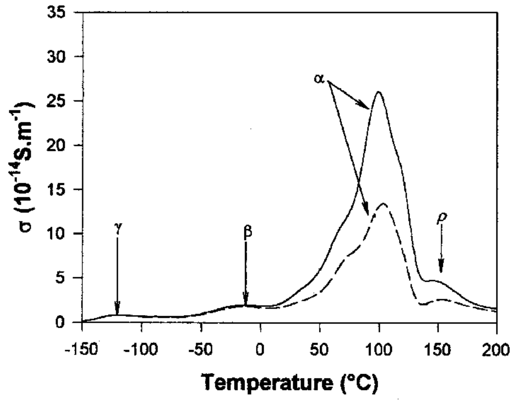

**Fig. 2** TSDC complex spectra, conductivity $\sigma$ *vs.* temperature, for the thermocured resin (dashed line) and for the photocured resin (full line) at 10 K min$^{-1}$ with $T_p$=150°C

peaks called $\gamma$ and $\beta$ are assigned to non cooperative local motions along the polymeric chains. This shows again that the resins obtained by the two different ways are identical in terms of local relaxation behaviour. At higher temperature, the $\alpha$ transition is observed and this transition is the dielectric manifestation of the glass transition. Because of cooperative rearrangements this transition appears at the same temperature for both systems as a succession of superimposed peaks. This indicates that the relaxation phenomena involved for these resins in the glass transition domain are complex. Nevertheless, it is clear that the magnitude of the $\alpha$ transition is not the same for the two resins. From the surface of the $\alpha$ peaks we can determine the polarization $P$ which is related to the number of units which are able to relax at the glass transition. The different values of $P$ and the characteristic temperatures of the transitions are reported in Table 1. Finally, at temperatures near the polarization temperature, we can observe the $\rho$ peak usually assigned to space charges [2].

**Table 1** Values of $T_g$, $\Delta h^*/R$ and $\Delta C_p$ obtained by DSC and values of $T_\gamma$, $T_\beta$, $T_\alpha$ and $P$ obtained by TSDC on the thermocured and photocured resins

| Materials | $T_g$ onset/ °C | $\Delta C_p$/ J g$^{-1}$ K$^{-1}$ | $\Delta h^*/R$/ kK | $T_\gamma$/ °C | $T_\beta$/ °C | $T_\alpha$/ °C | $P$/ μC m$^{-2}$ |
|---|---|---|---|---|---|---|---|
| Photocured resin | 120 | 0.305 | 130 | –120 | –20 | 100 | 34 |
| Thermocured resin | 100 | 0.22 | 57 | –120 | –20 | 100 | 22 |

Figure 3 now shows an example of the variations of the glass transition observed by DSC on the photocured resin for different cooling rates $q^-$ and for a unique value of the heating rate. As predicted by theory, the higher the cooling rate, the greater the value of the glass transition temperature. Following the method proposed by Moynihan *et al.* [6], Fig. 4 shows the linear variation of $\ln q^-$ with $1/T_f$ which leads to the

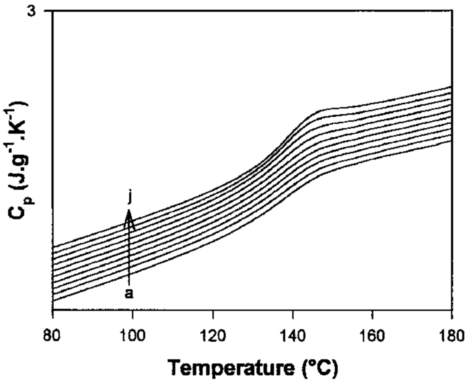

**Fig. 3** DSC heating curves (20 K min$^{-1}$) obtained for intrinsic cycles for the photocured resin for various cooling rates: a – 100 K min$^{-1}$, b – 50 K min$^{-1}$, c – 25 K min$^{-1}$, d – 20 K min$^{-1}$, e – 15 K min$^{-1}$, f – 10 K min$^{-1}$, g – 5 K min$^{-1}$, h – 2.5 K min$^{-1}$, i – 1 K min$^{-1}$ and j – 0.5 K min$^{-1}$.
The curves have been shifted vertically relative to each for shake of clarity

determination of $\Delta h^*$ (Eq. 4 and Table 1). In Table 1 we also report the values of the change in the specific heat capacity ($\Delta C_p$) at the glass transition.

All these results show that important differences exist between a thermally cured and a photochemically cured material. The value of the apparent activation energy is twice as great for the photochemically cured resin than for the thermally cured one. These variations are in good agreement with those observed on the polarization results. Because these two parameters are related to the relaxing units, their variations lead to the assumption that the number of relaxing units is more important in the photochemically cured resin than in the thermally cured one. By DSC, we observe a single glass transition temperature on a large glass transition domain. However, the different shoulders observed on the main α peak of the TDSC complex spectra show that we have different molecular relaxations for the same units.

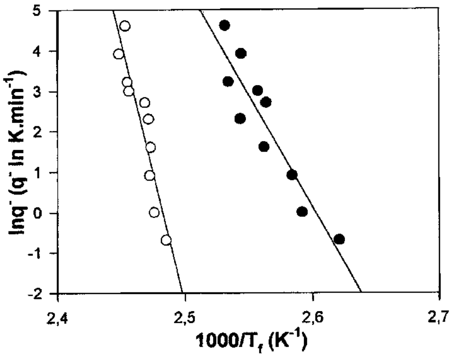

**Fig. 4** Variations of $1/T_f$ with $\ln q^-$ for the thermocured resin (full circles) and the photocured resin (open circles)

Because the molecular motions at the glass transition depend drastically on the free volume available for the relaxation, we have checked in a first approach if the value of the density for each material was able to explain our results. Unfortunately, both systems have practically the same density, i.e. 1.24±0.01. Therefore, the differences observed on the materials cannot be explained by a 'macroscopic' analysis of the relaxation phenomena. It is necessary to perform this analysis in terms of 'microscopic' assumptions. For the thermal way, the curing kinetics are very slow and allow the material to reach a stable structure. On the other hand, these kinetics are much faster for the photochemically cured resin and we can assume that the fastness of the reaction allows the crosslinking process but not the structural rearrangements. Then, in this case, the fact that the curing kinetics are very different in both materials can lead to the more likely assumption that the structure of the photochemically cured resin is farther from equilibrium than the thermally cured structure.

## Conclusions

We have shown that important differences exist between a thermally cured resin and the photochemically cured resin in term of molecular relaxation. Now, by changing the structure of the resins, the study of molecular relaxations on these materials of the same family will complete this first study in order to confirm our suggestions and will allow us to complete our investigations concerning the structural relaxation.

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