A STUDY OF PHOTO- AND THERMO-INITIATED POLYMERISED DIMETHACRYLATES BY THREE THERMAL ANALYSIS TECHNIQUES

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Abstract

Photo-initiated polymerisation of dimethacrylate oligomers provide an easy method for producing highly crosslinked polymer networks. The physical properties of the material are dependent on the polymerisation conversion value. The determination of this conversion value is quite difficult on the final product. The first step is to measure a characteristic temperature of the glass transition. The weakness of the DSC glass transition signal makes this measure unrealisable while the DMA tanδ peak is broad and weak. At the difference of these two thermal analysis techniques, TSDC gives an observable signal and a T_α temperature close to the glass transition temperature region. The bad sample preparation reproducibility observed was attributed to the high conversion rate.

Introduction

Photo-initiated polymerisation of multifunctional monomers provides an easy method for producing highly crosslinked polymer networks. The rapid curing and excellent physical properties of these networks have led to a growing demand and new applications for these materials. Comparatively with thermal polymerisation, photo-initiated polymerisation presents three main advantages: a curing reaction at room temperature, a very high reaction rate and an absence of solvent. For these reasons, photo-initiated polymerisation has found applications in many fields such as coating films [1], packaging industries, optical and dental materials [2–4].

Nevertheless, these high reaction rates and the resulting exothermic effect can be the cause of defects in the final material. These heterogeneities (generally a non-homogeneous conversion value) greatly alter the physical properties of the ultimate products and particularly the optic properties, which is a great problem for the design of a thick and op-

tically perfect material. Several parameters influence this kinetic and consequently the final conversion such as temperature, photo-initiator concentration, light intensity, and material thickness. The studies on these photo-initiated dimethacrylates were essentially performed using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) methods [5–6]. These studies have principally investigated the kinetic behaviour of the polymerisation [5] and the effect of temperature [6]. Lecamp *et al.* have shown that a maximum conversion was obtained at a temperature near 90°C. Below 90°C, the photochemical reaction completely stops when the glass transition temperature of the crosslinked material is reached. At temperatures higher than 90°C, thermal polymerisation can occur before photopolymerisation. In a photocalorimeter it is easy to manage the conversion value in isothermal conditions by measuring the photo-initiated polymerisation reaction heat flow during the polymerisation process [5]. A subsequent measure of the conversion value is quite difficult, effectively, the knowledge of a relation [7] between the glass transition temperature and the conversion value is one possibility to determine this parameter, but the weakness of the DSC glass transition signal makes this measure unrealisable. One goal of this work is to report the first results obtained by dynamic mechanical analysis (DMA) and thermally stimulated depolarisation currents analysis (TSDC). TSDC is used because of its low equivalent frequency (10^{-3} Hz) and its high sensitivity, which makes TSDC quite useful to detect and characterise the relaxations [8, 9]. Evolutions of the main α (dielectric manifestation of the glass transition) and secondary transitions with the cure on different photo and thermo-initiated polymerised dimethacrylate samples were studied here.

Experimental

Materials and samples preparations

Figure 1 shows the chemical formula of the reactants used. The average number of oxyethyl units in the dimethacrylate oligomer (Akzo, M=575 g mol^{-1}) was determined by ^{1}H NMR analysis and was found to be equal to 4.8. The photo-initiator
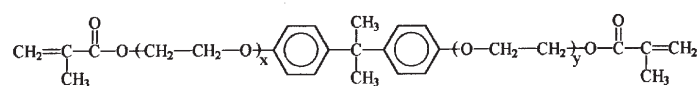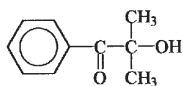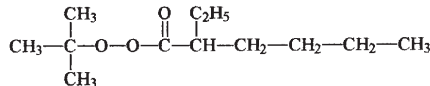

X = Y= 2.4

Dimethacrylate oligomer

Photo-initiator Darocure 1173   **Thermo-initiator TBPEH**

Fig. 1 Dimethacrylate oligomer, thermo- and photo-initiators

2,2-dimethyl-2-hydroxyaceto-phenone (Darocure 1173) was dissolved at the concentration 0.5% (w/w) in the dimethacrylate for 3 h. The photo-initiated dimethacrylate (PI-DM) samples (about 1 mm thickness with areas of 150 mm^2) were irradiated in a chamber at a temperature T=50°C during different times. The light source is a 100 W Hg vapour lamp, a neutral filter is used to obtain a 2.7 mW cm^{-2} light intensity at 365 nm and an electric shutter allows to control the irradiation time exposure.

The thermoinitiator a tertiobutyl-ethyl-2 perhexanoate (TBPEH) was dissolved at the concentration 0.25 mol l^{-1} in the dimethacrylate for 3 h. The thermo-initiated polymerised samples were annealed in a chamber at T=50°C for different periods of times.

Methods

DSC analysis was performed on a Perkin Elmer DSC7 calibrated with Indium. DMA was performed on a Metravib apparatus. The DMA samples were submitted to a traction-compression test with a frequency of 5 Hz. TSDC measurements were performed with an apparatus developed in our laboratory [10]. The sample is submitted to an electric field (E=10^6 V m^{-1}) during a period of time t_p (2 min) at a polarisation temperature T_p just above T_g (glass transition temperature). This allows the orientation of dipoles, the relaxation time of which is less than the period of polarisation. Then the polarisation is frozen in by decreasing the temperature with a constant cooling rate of 10 K min^{-1} with the electric field applied. The electric field is cut off and a short circuit is set up. Then, the increase of temperature (at a constant rate r=10 K min^{-1}) allows the gradual relaxation of different polarised units which results in a depolarisation current I (complex spectrum). Instead of I, the conductivity σ (in S m^{-1}) is used as a normalised quantity (σ= I/ES, where S is the surface of the sample).
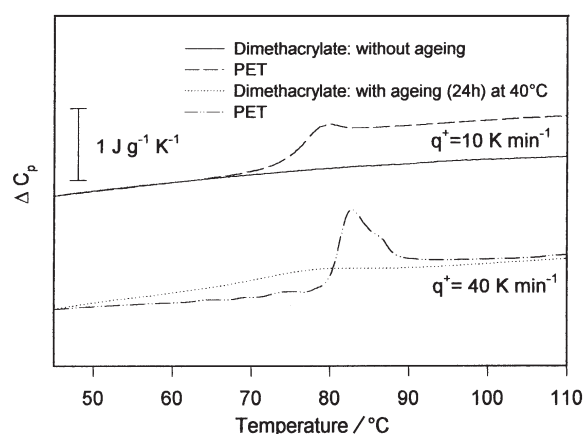

Fig. 2 Comparison between normalised DSC curves for amorphous PET and photo-initiated dimethacrylate (NB: q^+ is the heating rate). The PET samples are without ageing, they are annealed until 100°C before DSC scans. PI-DM samples had the same temperature and irradiation time (600 s, 50°C)

Results and discussion

DSC analysis

The comparison of the glass transition of a photo-initiated dimethacrylate sample (PI-DM) (irradiation time t_{ir}=600 s) with a reference thermoplastic (PET) clearly shows the weakness of the DSC signal for the dimethacrylate network (Fig. 2). Only ageing (T=40°C and t=24 h) and an important heating rate allow us to localise the glass transition of PI-DM but the determination of a characteristic temperature (the onset of T_g for example) is not realistic. For PI-DM sample, the glass transition seems to occur between 60 and 80°C.

TSDC and DMA analysis

Four different samples prepared under the same conditions were analysed by TSDC analysis between –150 and +100°C. First, focus was made to the –40 to +100°C temperature domain where the main transition appears (Figs 3a to 3c for three irradiation times). DMA curves show, for PI-DM with t_{ir}=600 s (Figs 4a and 4b), a weak diminution of the modulus E' and a broad and weak loss tanδ peak compared to the PET DMA curves.

A shift is observed between the three techniques for the characteristic temperatures (glass transition, α peak and tanδ peak). Indeed, the onset temperatures determined by TSDC, DSC and DMA are 60 [11], 70 and 75°C, respectively for PET and 40, 60 and 50°C for PI-DM. This shift can be attributed to various observed physical phenomena and different experimental parameters (equivalent frequency, heating rate).

At the difference of DMA, TSDC gives an observable signal and a T_α temperature close to the onset DSC glass transition temperature (T_α=61°C for TSDC and T'_α=105°C for DMA). So, the main TSDC transition was the dielectric manifestation of the glass transition and can be characterised by the temperature T_α of the peak maximum.
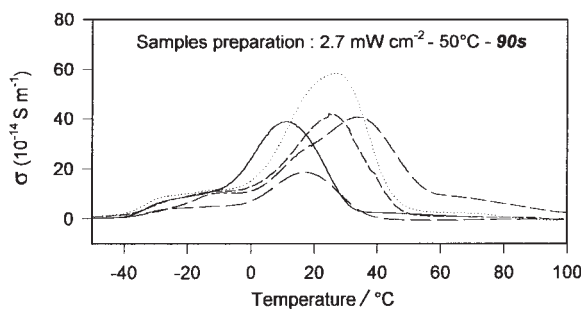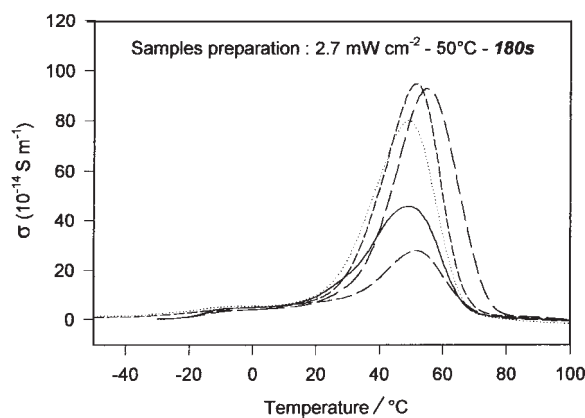

Fig. 3a TSDC spectra obtained for photo-initiated polymerised dimethacrylates (irradiation time 90 s); TDSC analysis parameters: E=10^6 V m^{-1} , T_p=80°C, T_d=50°C, q^+=10°C min^{-1}

Fig. 3b TSDC spectra obtained for photo-initiated polymerised dimethacrylates (irradiation time 180 s); TDSC analysis parameters: $E=10^6$ V m^{-1}, $T_p=80°C$, $T_d=50°C$, $q^+=10°C$ min^{-1}
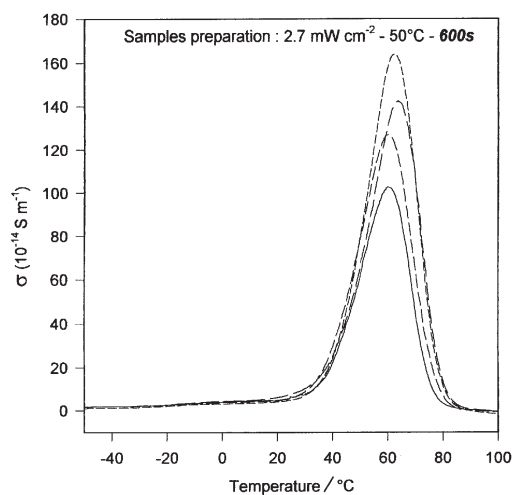

Fig. 3c TSDC spectra obtained for photo-initiated polymerised dimethacrylates (irradiation time 600 s); TDSC analysis parameters: $E=106$ V m^{-1}, $T_p=80°C$, $T_d=50°C$, $q^+=10°C$ min^{-1}

For samples prepared under the same experimental conditions, it appears that there is an important dispersion for T_α and σ_α (maximum of conductivity) (Fig. 3a for example). The data dispersion could be attributed to: i) the TSDC analysis procedure, ii) the material, iii) the network heterogeneity. The TSDC analysis of an amorphous thermoplastic shows generally a good reproducibility of the TSDC results [12]. So, the data dispersion must be attributed to the materials and/or their preparations. Fig-
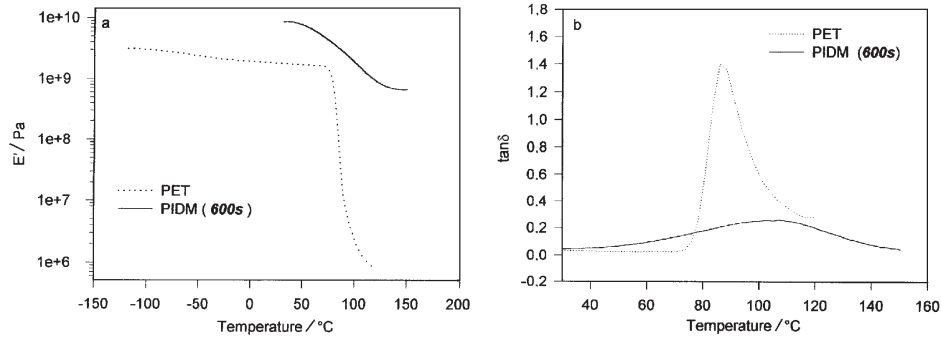
Fig. 4 Comparison between DMA curves for amorphous PET and PI-DM (irradiation time 600 s); DMA parameters: frequency: 5 Hz; $q^+=5°C\ min^{-1}$

ures 3a to 3c do not show a relation between the T_α and σ_α dispersions with increasing irradiation time (i.e. an increase of the conversion value). Evolution of T_α and $\sigma_\alpha$max *vs.* irradiation time is shown in Figs 5 and 6 respectively. Even if we do not know exactly the kinetic conversion of the material *vs.* irradiation time for our experimental conditions, the behaviour of the conversion follows the kinetic described by Lecamp *et al.* [7] for the same material prepared inside a photocalorimeter (unrealisable for our samples). Two domains exist: for short time (0<*t*<100 s), a high rate conversion process occurs with 80% of the conversion while for longer time
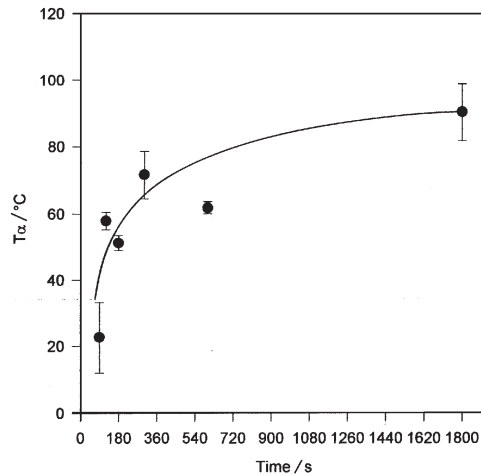

Fig. 5 T_α *vs.* irradiation time for PI-DM samples; Fit curves is obtained by Table curve 2D® Jandel scientific

(t>100 s), a weak rate conversion process occurs. So, the T_α increase with irradiation time is due to the increase of the conversion values which enhances the network rigidity. This behaviour could explain the highest T_α dispersion for t=90 s (Fig. 3a). Effectively, for this time, the high conversion rate leads to bad sample preparation reproducibility but the high dispersion for an irradiation of 1800 s impeded us to be so
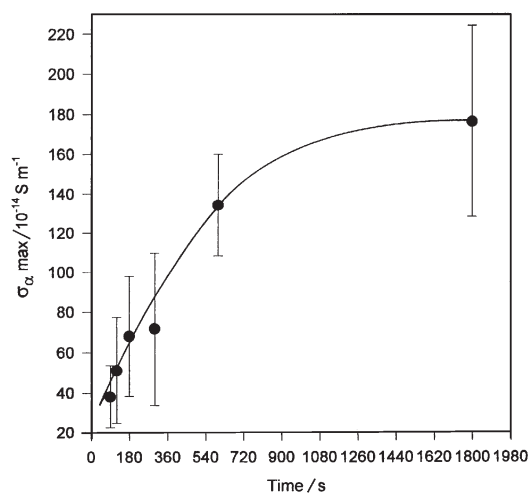

Fig. 6 Conductivity *vs.* irradiation time for PI-DM samples. Fit curves is obtained by Table curve 2D® Jandel scientific
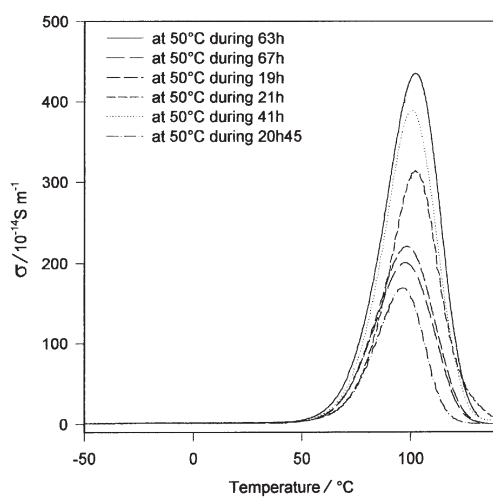

Fig. 7 TSDC spectra obtained for thermo-initiated polymerised dimethacrylates. TDSC analysis parameters: E=10^6 V m^{-1}, T_p=120°C, T_d=50°C, q^+=10°C min^{-1}
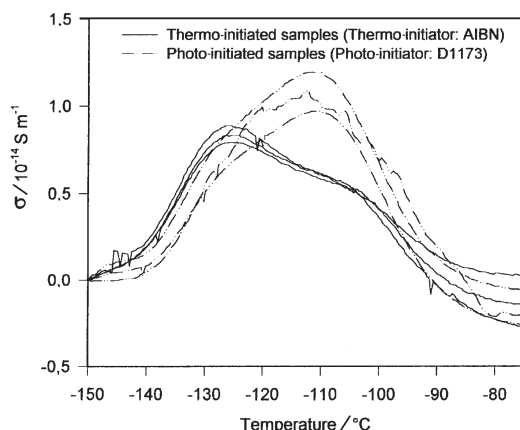
Fig. 8 Comparison between TSDC spectra of thermo-initiated polymerised (at 50°C)
and photo-initiated polymerised dimethacrylates (2.7 mW cm^{-2}; 50°C; 600 s) in
the β region

affirmative. Figure 6 shows the increase of the conductivity with irradiation time. This behaviour is similar to those of T_α temperature but cannot be explained.

Six thermo-initiated polymerised dimethacrylate (TI-DM) samples were obtained by different curing periods of time. TSDC spectra (Fig. 7) show the same T_α value (i.e. same conversion value) (T_α=100°C) for the different samples. We can notice that these materials have a higher T_α value than for PI-DM. Supposing, as shown by [7], that a linear relation exists between the conversion and the T_α temperature, we can conclude that the TI-DM material have a higher conversion value than PI-DM. Nevertheless, it is surprising to observe an important dispersion in the conductivity values for the three samples with the same curing time ($t \approx 20$ h). No dependence is found between the maxima of conductivity and the curing time (included between 20 and 67 h). In the –150 to –70°C temperature region, one can observe the β relaxation peak (Fig. 8). This peak is attributed to local motions of dipoles. The temperature and the shape of the peak are quasi-identical for the different PI-DM whatever the sample preparation and the conversion value is. The β peak shape of TI-DM appears different and seems to be composed of two peaks. The influence of the initiator on the local motions that occur at T_β has not yet explained.

Conclusions

TSDC analysis, at the difference of DSC and DMA, allows a good determination of the glass transition temperature. Indeed, the TSDC peak is clearly observed and the reproducibility of the T_α temperature is correct. A subsequent measure of the conversion value C is now possible. Nevertheless, the reproducibility of the σ peak heights is low for thermo- and photo-polymerised samples and no dependence of the reproducibility with the conversion is observed. So, our TSDC experimental condi-

tions do not allow to decide which method (UV or thermal curing) leads to better results in terms of network homogeneity. The increase of the conductivity as a function of irradiation time has not yet explained and need further investigations.

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