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Polymer Communication

Indications of micro-vitrification during chainwise cross-linking polymerisation

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Abstract

This communication presents results from dynamic mechanical analysis and measurement of charge-recombination luminescence showing that the vitrification process during isothermal cure of an acrylate resin appears to proceed in two steps. Glass formation, as determined by charge-recombination luminescence, is found to occur much before macroscopical gelation and vitrification are detected in dynamic mechanical analysis. This suggests the presence of a micro-vitrification transition in addition to the analogous micro-gelation process which has been reported in diacrylate polymerisations. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Gelation; Vitrification; Micro-transition

1. Introduction

Chain-wise cross-linking polymerisation reactions of difunctional or polyfunctional acrylates have a number of features that set them apart from their simpler and more easily understood step-wise counterparts, e.g. epoxy resins [1,2]. Chain-wise reacting systems generally have high functionality and reactivities that change as the reaction proceeds due to simultaneous homopolymerisation and network formation, which in combination with the localised initiation of the polymerisation leads to highly heterogeneous systems and low gel point conversions [1,3,4]. Both chain-wise and step-wise reacting systems undergo phase changes during network formation. The reacting mixture is transformed from a liquid to a solid, passing through the gelation (liquid to rubber) and vitrification (rubber to glass) transitions [1,5]. For step-wise reacting systems, simple statistical theories that well describe the relationship between the progress of the polymerisation reaction and the transitions in properties have been developed [6–8], and the evolution of properties has been thoroughly investigated experimentally [5,9].

In the case of chain-wise reacting systems, the heterogeneity and other features that have to be considered require the use of more complex, three-dimensional and/or kinetically based theories and simulations [3,4,10,11]. These theories predict the structure build-up during chain-wise cross-linking to proceed in several steps. At very low conversions, a limited number of small, densely cross-linked clusters of high molar mass arise. Links then form between the clusters until macroscopical gelation occurs. At this point, the conversion typically is 10–15%, which means that most of the monomer is still unreacted. During the rest of the reaction, the monomer units are gradually incorporated into the growing network until the glass transition temperature (T_g) of the system reaches the reaction temperature and vitrification sets in, or, if the reaction temperature is above the ultimate T_g of the system, all of the functional groups have reacted.

Due to the small size and low concentrations of the structures involved, the heterogeneity in chain-wise cross-linking polymerisation has been difficult to quantify experimentally. However, micro-gelation in chain-wise cross-linking polymerisation has recently been verified [12,13]. Nanometre-sized particles have been detected, isolated and found to be densely cross-linked with conversions of 60–70% [12].

The presence of trapped radicals early in the reaction has pointed to the presence of regions of high cross-link density/low mobility while the bulk of the system is still in the liquid or rubbery state [14]. While the significance of this was not commented upon by these authors, the observations of

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low mobility and high cross-link density suggest that the clusters undergo not only micro-gelation [12,13], but also micro-vitrification when the cure temperature is below the ultimate T_g. It is the purpose of this communication to present experimental findings supporting this view. A dimethacrylate system is investigated, and the macroscopical and microscopical cure behaviour examined using dynamic mechanical analysis and charge-recombination luminescence, respectively. In particular, it is shown that this micro-vitrification occurs before macroscopic gelation.

2. Experimental

The monomer, tetra-ethoxylated bisphenol A dimethacrylate, and the thermal initiators, azobisisobutyronitrile (AIBN) and tert-butyl hydroperoxide, were obtained from Aldrich.

Dynamic mechanical analysis was performed in a Rheometrics RDS 2, using parallel plates and samples of approximately 4 mm diameter and 1.5 mm thickness. The experimental procedure has been described elsewhere [9,15]. Samples of acrylate with 1.5% by weight of initiator were placed in the instrument, and the complex modulus was measured at regular intervals throughout the cure process using a multiwave technique involving superposition and decomposition of the signal, which permitted data at several frequencies to be collected simultaneously. The strain was 0.2% and the frequencies 0.25, 0.5, 1, 2 and 4 Hz. To obtain reasonable rates of reaction, cure at 130°C was performed using the peroxide initiator, whereas cure at 60°C was carried out with AIBN.

Charge recombination luminescence (CRL) was measured in a set-up composed of a sample hot-stage, covered by a quartz window, and placed in a light-tight box with a Thorn EMI 9816B photomultiplier tube mounted in the lid. Photon counting was carried out by a SR400 2-channel photon counter (Stanford Research Systems). Details of the experimental procedure may be found elsewhere [16,17]. The CRL during cure was measured by repeatedly irradiating the acrylate sample with a Kulzer Duralex UV-300 fibre optic wand for 60 s. After each irradiation, the shutter of the photomultiplier was opened with a delay of 5 s, and the initial intensity of emitted light, I_0, recorded as the number of photons emitted over the following 0.5 s. AIBN was used as initiator for cure at both 130 and 60°C in order to limit the effect of the UV irradiation during CRL measurement on the initiation rate of polymerisation.

3. Results and discussion

3.1. Macroscopic rheology

The macroscopical development of structure and properties during cross-linking polymerisation can conveniently be characterised using dynamic mechanical analysis [9,15]. This technique measures the overall, average properties of the reacting system and is thus not particularly sensitive to any microscopic heterogeneities present. The dynamic mechanical behaviour of the acrylate system during cure at temperatures above and below the ultimate glass transition temperature of the system is depicted in Fig. 1. Cure at 130°C involves macroscopical gelation, occurring after about 700 s, as indicated by the rise in G', and the beginnings of vitrification, evidenced by the onset of a

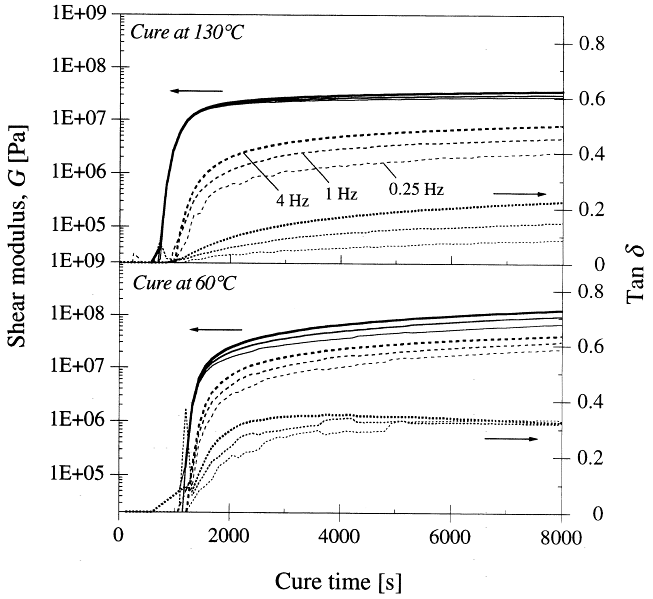

Fig. 1. G' (solid lines), G'' (dashed lines) and tan δ (dotted lines) measured at 0.25 Hz (fine lines), 1 Hz (medium lines) and 4 Hz (heavy lines) during cure of the acrylate at temperatures above and below the ultimate T_g.

frequency-dependence in G' and the rise in tan δ [15]. At 60°C, the material exhibits macroscopic gelation after 1000 s, and begins to vitrify after 1500 s (G' becomes frequency dependent). Vitrification is more complete at this temperature, as shown by tan δ exhibiting a maximum after 2500 s and G' rising to a higher value at the end of the cure. It is worth mentioning that the overall degree of conversion of the system on vitrification at 60°C is known to be 50–75% [15], which is similar to what has been reported for micro-gel particles [12]. It should be emphasised that no evidence for either micro-gelation or micro-vitrification may be obtained from the rheological measurements. This may only be detected by other techniques.

3.2. Charge recombination in glassy solids

Charge-recombination luminescence (CRL) is weak light emitted from solid materials following UV irradiation. The UV irradiation ionises the sample and creates separated charges that subsequently may recombine under light emission. If the mobility in the system is low, the recombination is delayed and the light emission goes on for seconds to minutes after the initial irradiation. This phenomenon has been thoroughly investigated in epoxy/amine systems, and it has been shown that CRL is observed only when the material is in the glassy state [16–18]. Fig. 2 presents dynamic mechanical data and CRL intensity as a function of temperature for a fully cured acrylate sample. As can be seen, the system has a T_g of about 110°C (tan δ peak). Above this temperature, the CRL intensity is constant at a value corresponding to the background level. On cooling below T_g, there is a strong increase in CRL intensity, which confirms that CRL only arises when the system is vitrified.

The identity of the species responsible for CRL has been a topic of very active research [18]. In the study of cured epoxy resins containing aromatic amine groups either in the resin or hardener, it was found that the CRL arose, after photoionization of the aromatic amine, by the recombination of electrons trapped in the glassy matrix with the N-centred cation. The electrons which were within the Coulombic field of the cation were able to recombine immediately, producing an excited state and thus luminescence, while the trapped charge resulted in thermoluminescence when the sample was subsequently heated. In an aromatic ether system, e.g. the diglycidyl ether of bisphenol A cured with an aliphatic amine, the cation centre is less well defined, but it has been found that CRL is observed only when the system is in the glassy state [17]. No effect of gelation on the incidence or intensity of CRL was observed. The tetra-ethoxylated dimethacrylate of bisphenol A studied here is analogous to the latter system in that there is no aromatic amine cation centre, but still CRL is observed. The most important observation from these earlier studies which is relevant to the present system is that it is impossible to observe CRL unless the system has reached the glassy state [17,18]. It is also possible to distinguish CRL from photoluminescence by the much longer duration (from tens of seconds to minutes) of the CRL.

The CRL intensity as a function of time during isothermal cure at two temperatures is shown in Fig. 3. As a comparison, data for cure of an epoxy system below the ultimate T_g (from Ref. [17]) is included. For cure of the acrylate at

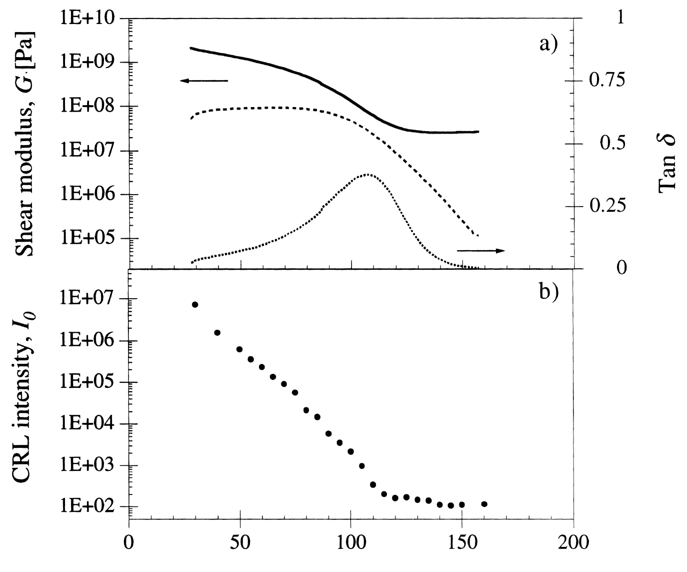

Fig. 2. (a) G' (solid lines), G'' (dashed lines) and tan δ (dotted lines) at 1 Hz. (b) Charge-recombination luminescence intensity (circles) as a function of temperature measured on cooling of a fully reacted acrylate sample.

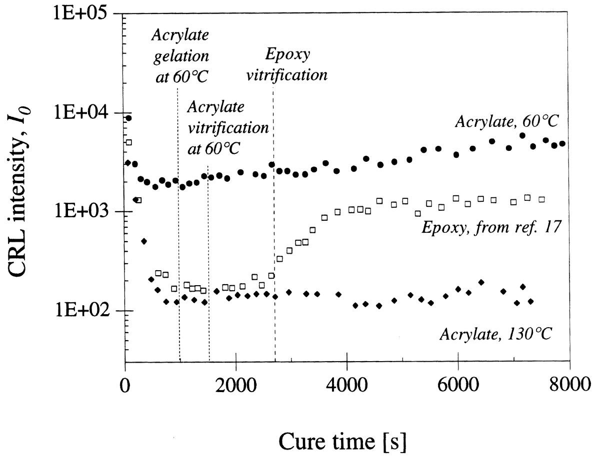

Fig. 3. Charge-recombination luminescence intensity as a function of cure time during cure of the acrylate system at temperatures above and below the ultimate T_g. Data for an epoxy-amine system from Ref. [17] are included for comparison. The gel- and vitrification times indicated are from dynamic mechanical measurements.

130°C, the intensity is initially high, due to recombination of trapped charges in the sample during the heating-up (thermoluminescence), but as the cure temperature is reached the intensity drops to the background level. This is a further indication that the gel state does not give rise to any significant amounts of CRL. On cure at 60°C, a completely different behaviour is observed. Here the CRL intensity never drops to background level after the heating-up period. Instead, the intensity falls to about 2000 and then grows steadily during the rest of the cure process. The data for the epoxy in Fig. 3 show that for this system, the CRL intensity remains at the background level until vitrification commences. The fact that significant CRL intensities are observed in the acrylate already at the beginning of the reaction, prior to macroscopical vitrification, is thus a strong indication that glassy material is formed early in the cure process.

It is reminded that the CRL measurement involves irradiating the sample with UV light, which has the potential of accelerating the cure reaction. The peroxide initiator was found to be very sensitive to UV light, which is why AIBN was used for all CRL measurements. For AIBN, experiments performed in a UV-rheometer [15] under constant UV irradiation showed that at 60°C the macroscopical gelation and vitrification times decreased about 300 s. Since the sample is only intermittently irradiated in the CRL experiments, the change should be well below 300 s in this case.

4. Conclusions

A comparison of results from dynamic mechanical analysis and measurement of charge-recombination luminescence shows that the vitrification process during isothermal cure of an acrylate resin appears to occur in two steps. Vitrification, as determined from the presence of a significant CRL intensity, begins as soon as the sample reaches the cure temperature. Dynamic mechanical analysis shows that macroscopical gelation and vitrification do not occur until much later. This is interpreted as the sample undergoing micro-vitrification prior to the macroscopic transitions being observed.

Acknowledgements

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