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Structural investigation of e-beam cured epoxy resins through solid state NMR

Sabina Alessi [a], Alberto Spinella [b], Eugenio Caponetti [b,c], Clelia Dispenza [a,*], Giuseppe Spadaro [a]

[a] Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy
[b] Centro Grandi Apparecchiature—UniNetLab, Università degli Studi di Palermo, Via F. Marini 14, 90128 Palermo, Italy
[c] Dipartimento di Chimica "S. Cannizzaro", Università degli Studi di Palermo, Viale delle Scienze pad. 17, 90128 Palermo, Italy

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ABSTRACT

In this paper the network structure of e-beam cured DGEBF based epoxy resins is investigated. Two epoxy systems, having different reactivity and cured in different process conditions, were analyzed through solid state NMR spectroscopy. The analysis shows that the more reactive system has higher cross-linking density and higher uniformity of network distribution. Similar information were obtained, in a previous work, on the same systems through dynamic mechanical thermal analysis. It is worth noting that unlike DMTA tests, which interfere with the molecular structure of the analyzed material, due to the heating during the analysis itself, more reliable information, without any artefact, are obtained by solid state NMR, carried out at constant room temperature.

1. Introduction

The use of ionizing radiation for the production of composite materials with polymer matrices as an alternative to conventional thermal curing can be justified by its advantages, mainly lying in the not thermal activation of the curing reactions and in the short processing times (Lopata et al., 1999; Woods, 2000; Singh, 2001). A drawback of this process, related to the use of the low temperature as cure temperature, can be the occurring of vitrification phenomena in the polymerizing systems. Indeed it is known that curing reactions cause the increase of the glass transition temperature of the polymerizing material that soon approximates and overcomes the low cure temperature. This strongly reduces the mobility of the molecular chains and slows down the rate of further curing reactions, which are hindered by the low reactive species diffusion. This effect can imply the formation of structures consisting in clusters with different cross-linking densities. This was already shown and discussed in previous papers, (Alessi et al., 2005, 2007; Spadaro et al., 2005) where the study of the molecular structure of the e-beam cured materials has been carried out by dynamic mechanical thermal analysis (DMTA). In these papers it was shown that DMTA of samples cured at low temperatures presented a very large relaxation peak, starting from very low temperature, according to the formation of a not uniform molecular structure. Furthermore DMTA curves presented a second, more narrow relaxation peak at higher temperature, which was mainly attributed to the occurring of a post-irradiation thermal curing due to the DMTA test itself, when the test temperature is next to that one of the first relaxation peak and the vitrification phenomena are overcome.

Dynamic-mechanical–thermal analysis is one of the main techniques used for the investigation of the supra-molecular structure of polymeric systems and it is very effective in order to observe their viscoelastic nature. Nevertheless DMTA has the inherent limit that the heating interferes with the original structure of the material, giving rise to artefacts, which in principle do not allow to have exact information about the structure of the investigated material.

A more reliable and alternative technique is represented by solid state nuclear magnetic resonance spectroscopy (ss-NMR). This experimental methodology has been used in the last decades as a powerful tool to characterize the structure, the conformation and the mobility of the molecular chains of cross-linked systems without altering the investigated structure. In particular it allows to understand the relationships between physical properties and molecular motions in solid polymers (Fry and Lind, 1988; Tonelli, 1995; Brady et al., 2005). In fact with the development of advanced techniques such as cross polarization (CP), magic angle spinning (MAS) and high power dipolar decoupling (HPDD), it is possible to obtain high resolution spectra for solid samples. Solid-state NMR spectroscopy has been extensively used to study the structure and dynamics of polymers and polymer blends (Guo, 1997). As solid-state NMR data are sensitive to intermolecular as well as intra-molecular interactions, they can provide

* Corresponding author. Tel.: +39 91 238637210; fax: +39 91 23860841.
E-mail address: clelia.dispenza@unipa.it (C. Dispenza).

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important information about both chain dynamic and packing in polymer systems.

In this paper the study of the molecular structure of radiation cured epoxy resin systems is carried out by solid state NMR spectroscopy. The aim is to have information about the material structure without inducing modifications during the test itself. In particular two epoxy based systems cured in very different experimental conditions have been investigated, in order to obtain significantly different molecular structures, able to emphasize the response of solid state NMR analysis.

2. Experimental

The epoxy resin analyzed was the bis(4-glycidyloxyphenil) methane generally known as diglycidylether of bisphenol F (DGEBF), supplied by Aldrich (160–170 g/eq), and the initiator was an iodonium salt, Cumyltolyliodonium tetra(pentafluorophenil) borate, supplied by Rhodia Silicones.

E-beam irradiation was carried out in closed steel molds (dimensions of the samples $150 \times 150 \times 4\ mm^3$) at the ISOF-CNR laboratory in Bologna with the 12 MeV Vickers type linear accelerator (Fuochi and Lavalle, 2002). Two blends with different initiator contents, different irradiation doses and different dose rates were prepared. The sample A was synthesized using 0.1 phr (per hundred parts of epoxy resin) of iodonium salt, an irradiation dose of 80 kGy and a dose rate of 84 kGy/h. The sample B was synthesized using 1 phr of iodonium salt, an irradiation dose of 150 kGy and a dose rate of 840 kGy/h. The details related to both the preparing procedure of the blend and the measure of the temperature during irradiation are described elsewhere (Alessi et al., 2005).

^{13}C Cross Polarization—Magic Angle Spinning Nuclear Magnetic Resonance (^{13}C $\{^1H\}$ CP-MAS NMR) spectra were obtained at room temperature through a Bruker Advance II 400 MHz (9.4 T) spectrometer operating at 100.63 MHz for the ^{13}C nucleus with a MAS rate of 13 kHz, 1024 scans, a contact time of 1.5 ms and a repetition delay of 3 s. The optimization of the Hartmann–Hahn condition (Hartmann and Hahn, 1962) was obtained using an adamantine standard. All samples were placed in 4 mm zirconia rotors with KEL-F caps. The proton spin–lattice relaxation time in the laboratory frame T_1H was determined with the saturation recovery pulse sequence (Alamo et al., 2002) with delay times τ ranging from 0.01 to 3 s. The proton spin–lattice relaxation time in the rotating frame $T_{1\rho}H$ was determined with the variable spin lock (VSL) pulse sequence (Lau and Mi, 2002) using delay times ranging from 0.1 to 7.5 ms and a contact time of 1.5 ms. The T_{CH} values were obtained through variable contact time (VCT) experiments (Conte et al., 2004) using contact times ranging from 0.05 to 7.0 ms.

3. Results and discussion

As already reported, e-beam cured materials can be produced with significant different molecular structures and properties, depending on the experimental conditions (Raghavan and Baillie, 2000; Alessi et al., 2005, 2007, 2010; Spadaro et al., 2005). In fact radiation curing, even starting from room temperature, can produce in the polymerizing resin thermal effects, depending on both the chemical formulation and the process parameters. Among others, the irradiation dose rate and the initiator content can significantly affect the heat evolution rate and hence the temperature of the system during irradiation. The resulting thermal profile of the system during irradiation strongly affects the kinetics of curing and then the final molecular structure of the cured material. In particular the increase of both the initiator content and the irradiation dose rate causes an increase of the heat evolution rate, which in turn produces a rise of the temperature in the polymerizing system, due to the rate increase of both the absorption of the radiating energy and the evolution of the curing reactions exothermic heat. Ultimately, during radiation curing, these phenomena cause the occurrence of a thermal treatment, which in some cases can be a proper thermal curing.

On the basis of these considerations the system used for this investigation was cured at two different conditions: low (sample A) and high (sample B) values of both initiator concentration and dose rate. For sample A the low cure temperature (Tmax$=50\ ^\circ C$) causes the occurring of only radiation curing, while for sample B also thermal curing occurs (Tmax$=220\ ^\circ C$), with the final result of obtaining materials with both cross linking densities and uniformities very different.

The molecular structure of the two materials were investigated by sold state NMR.

First of all, the ^{13}C $\{^1H\}$ CP MAS NMR spectra of both epoxy systems, reported in Fig. 1, evidence that sample A still presents a well defined epoxy CH terminal group, while for sample B the polymerization is almost quantitative, as revealed by the absence of the same group.

Nuclear relaxation times were obtained for the two samples in order to correlate the dynamic differences of the two polymeric networks with the different synthesis conditions.

It is known that the spin lattice relaxation times in the rotating frame and in the laboratory frame, $T_{1\rho}H$ and T_1H, are sensitive to the molecular motions, which occur in the kHz and in the MHz regions, respectively. In particular, they are inversely proportional to the spectral density of motions in the region from a few to tens of nanometers. (Boyer, 1968; Fawcett, 1996; Ferrar and Becker, 1971; Campbell and Dwek, 1984).

The T_1H, $T_{1\rho}H$ values obtained for each peak of the two ^{13}C spectra as function of the chemical shift are reported in Fig. 2 together with the chemical shift assignments.

In the sample A both T_1H and $T_{1\rho}H$ values vary in wide ranges, and in particular from 1.0 to 7.1 s for T_1H and from 4 to 6.7 ms for $T_{1\rho}H$. On the contrary the sample B shows both T_1H and $T_{1\rho}H$ values ranging in shorter intervals, from 2.3 to 4.9 s and from 5.5 to 6.5 ms, respectively, thus implying that sample A has more than one zone with different dynamical behaviors. High T_1H values can be associated to zones at high cross-linking density, while low T_1H values can be associated to zones at low cross-linking density. On the contrary, the homogeneity of the correspondent relaxation times

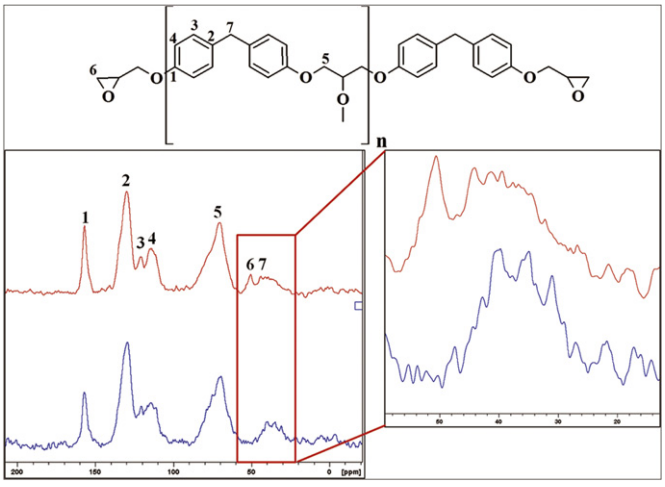

Fig. 1. ^{13}C $\{^1H\}$ CP MAS NMR spectra of the radiation cured samples.