

Coatings obtained through cationic UV curing of epoxide systems in the presence of epoxy functionalized polybutadiene

M. SANGERMANO, G. MALUCCELLI, R. BONGIOVANNI,
G. GOZZELINO, F. PEDITTO, A. PRIOLA

*Dipartimento di Scienza dei Materiali, e Ingegneria Chimica, Politecnico di Torino,
C.so Duca degli Abruzzi 24, 10129, Torino, Italy*

E-mail: priola@fenice.polito.it

The cationic photopolymerization of a biscycloaliphatic and a di-glycidyl epoxide monomer was investigated in the presence of an epoxy hydroxy functionalized polybutadiene (PBE). Triphenylsulfonium hexafluoroantimonate was used as photoinitiator. The kinetics of UV curing, in the presence of the additive, was determined via FT-IR analysis, showing an increase of the rate of photopolymerization and of the final epoxy groups conversion. Comparison experiments were performed with hydroxy functionalized polybutadiene. Evidences are obtained that PBE is incorporated via a copolymerization reaction involving the epoxy groups and via a chain transfer reaction involving the OH groups. The investigation of the properties reveals a flexibilization effect due to the presence of the additive, evidenced by a sharp decrease of T_g of the cured films.

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1. Introduction

The UV curing process is a polymerization technique in which radiations induce a fast transformation of a liquid monomer into a solid polymer. Radical or cationic species are generated by interaction of UV light with a suitable photoinitiator [1]. Onium salts initiate the cationic curing process by generating very strong Brønsted acids upon photodecomposition [2].

Cationic photoinduced process presents some advantages over the radical one [3]; in particular lack of inhibition by oxygen, low shrinkage, good mechanical properties of the UV cured materials and good adhesion properties to various substrates. In addition, the monomers employed are generally characterized by low irritation and toxicity properties. Different types of monomers and oligomers have been proposed and reported in literature [4, 5]; among them mainly epoxides are currently used in industry because of their availability and good properties after curing. One of the main limitations to the use of UV curable epoxy resins lies in their relatively low reactivity, especially when compared to the widely used acrylate based resins [6].

Biscycloaliphatic diepoxides are known to be more reactive than glycidyl ethers, because of the strain of the adjacent cyclohexane ring [7]; for this reason they are the most used in today's industrial cationic photocuring applications [8].

In such network forming systems, polymerization proceeds rapidly in the first step, then polymerization markedly slows down but can still occur as monomer diffuses to the fixed propagating sites within the swollen

gel. However, as the T_g of the network approaches the curing temperature vitrification sets in. At this point diffusion of the monomers is prevented and polymerization actually stops before all the polymerizable groups are consumed. As a result a large amount of epoxy groups can remain unreacted. While such resins have excellent solvent resistance, their rigid structures contribute to their rather poor elongation and flexibility characteristics. In many coatings applications there is a need for tough, flexible materials having considerable elongation at break. For this reason, it is desirable to find ways of obtaining good mechanical characteristics of UV cured epoxy coatings, together with high flexibility.

In the literature systems based on the photopolymerization of epoxy monomers in the presence of vinyl ethers or propenyl ethers are reported; they show an increase of the UV curing kinetics [9, 10]. Another way to obtain a fast and complete polymerization consists of introducing reactive plasticizing agents. They delay the point of vitrification by increasing the mobility of the chains, so that the polymerization rate remains high and a higher epoxy group conversion is achieved [11].

The presence of a plasticizing agent linked to the epoxy network increases the flexibility of the cured product and the impact resistance giving rise to a good balance of the mechanical properties typical of the epoxy resins, and of the resilience behaviour.

In a previous paper is reported the use, as plasticizing agent, of epoxide soybean oil [12]; evidences are given that a true copolymerization occurs between the different types of epoxy groups. In this work we

investigate the use of epoxy functionalized polybutadienes as modifying agents of epoxy systems under cationic UV curing conditions.

The epoxidation of liquid polybutadienes has been studied by different authors [13–15] who have investigated the kinetics of the reaction, the reactivity of the double bonds and the effect of the experimental conditions on the epoxidation degree. In this paper we report the results obtained by using a typical epoxy functionalized polybutadiene as additive of epoxy systems, considering both the kinetics of photopolymerization and the properties of the cured products.

2. Experimental

2.1. Materials

The epoxy difunctional monomers were: 1,4-cyclohexanedimethanol diglycidyl ether (DGE) from Aldrich and 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (CE), kindly supplied by Union Carbide. A sample of hydroxy functionalized polybutadiene (PBOH, from Aldrich) was used; $M_n = 1200$; 55% 1,4 trans; 20% 1,4 cis; 25% 1,2; hydroxyl number 1.7 meq/g. The homologous epoxidized polybutadiene (PBE) was employed, containing about 20% of epoxidized double bonds (epoxide equivalent = 260); on the basis of the literature data [15] we can assume that the epoxy units are mainly of 1,4-trans type. Triphenylsulfonium hexafluoroantimonate (PI), from Union Carbide, was used as the cationic photoinitiator in a concentration equal to 2 wt%. The structures of the epoxy monomers and photoinitiator are reported in Table I.

2.2. Film preparation

The photocurable mixtures were spread on a glass slide with a calibrated wire-wound applicator to obtain a

thickness of about 100 μm . The curing reaction was performed by UV irradiation with a medium pressure Hg lamp (Italquartz, Milano, Italy); the light intensity at the film surface was 250 W/m^2 . The irradiation was stopped when a constant epoxy groups conversion was achieved, as determined by FTIR measurements (see below). The samples, after irradiation, were stored for one night and then put for 15 minutes in a closed system saturated with a 5% v/v water/ammonia solution vapors, in order to neutralize the acidic species.

2.3. Film characterization

The degree of epoxy groups conversion was calculated coating the mixture on a KBr disk, and measuring the ratio of the corresponding IR absorbance (respectively at 847 cm^{-1} for the DGE epoxy monomer and 795 cm^{-1} for the CE monomer) before and after UV exposure. The kinetic curves were obtained by measuring the decrease of the epoxy absorption band, after different irradiation time. A Genesis Series ATI Mattson (USA) spectrometer was used.

The Gel Content of the films was determined by measuring the weight loss after 20 hours treatment at room temperature with chloroform. DSC measurements were performed with a Mettler DSC30 (Switzerland) instrument, equipped with a low temperature probe. Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at the frequency of 1 Hz in the tensile configuration.

3. Results and discussion

3.1. Photopolymerization reaction

After one minute of irradiation at 250 W/m^2 intensity, and in the presence of arylsulphonium photoinitiator, the DGE monomer gave a tack-free film. About 10% of soluble product was extracted by chloroform (Table II).

TABLE I Structure of the epoxy monomers and photoinitiator

| Epoxy monomers | |
|---|------|
| | |
| (DGE) | (CE) |
| Photoinitiator | |
| $\text{Ph}_3\text{S}^+\text{SbF}_6^-$ (PI) | |

TABLE II Properties of the UV cured films obtained from DGE-PBE mixtures

| Sample | Gel content (%) ^a | Conversion (%) ^b |
|-----------------------|------------------------------|-----------------------------|
| Pure DGE | 90 | 55.8 |
| Pure PBE | 95 | 48 ^c |
| DGE:PBE 90 : 10 wt/wt | 98 | 67.5 |
| DGE:PBE 80 : 20 wt/wt | 98 | 77.9 |
| DGE:PBE 70 : 30 wt/wt | 97 | 85.3 |
| DGE:PBE 50 : 50 wt/wt | 98 | 98.8 |

^aAfter 20 hours of CHCl_3 treatment.

^bEpoxy groups final conversion calculated on the basis of the IR peak at 847 cm^{-1} .

^cCalculated on the basis of the IR peak at 910 cm^{-1} .

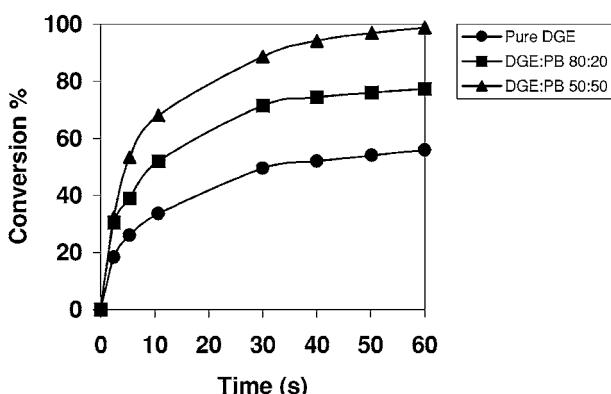


Figure 1 Kinetic curves of Pure DGE (●) compared with the mixture DGE:PBE 80 : 20 (■) wt/wt and DGE:PBE 50 : 50 wt/wt (▲).

The kinetic curve, related to pure DGE (Fig. 1), shows that at the beginning the kinetics of polymerization is high, then an asymptotic behaviour is observed. This trend is typical of cationic photopolymerization [16]; it was attributed to the fact that the propagation rate constant of the system is strongly affected by the molecular mobility of the growing chain. At high epoxy group conversion a highly crosslinked network is formed which hinders the mobility of the chains; when this point is reached the reaction stops. In the pure DGE photopolymerization, this point corresponds to about 55% epoxy groups conversion.

The addition, to the mixture, of PBE in different amounts ranging between 10 to 50 wt%, induces a clear increase of the curing rate and of the epoxy groups final conversion (Fig. 1). This effect is evident from the data reported in Table II; in the presence of 20 wt% of PBE the final epoxy group conversion reaches 78%; in the presence of 50 wt% of PBE the conversion is almost complete. Moreover the gel content is very high (97–98%), in the presence of PBE, indicating that PBE is linked into the polymer network. Considering the epoxy equivalent of PBE, we can calculate that about 5 epoxy groups per PBE molecule are present; therefore PBE can act as a crosslinker, thus modifying the tridimensional polymer network. Moreover PBE contains also hydroxyl groups; they can interact with the cationic growing chains via a chain transfer reaction, as reported in the literature [17–19]. It was not possible to follow the consumption of the epoxy groups of the PBE in the photocurable mixture, because they are overlapped with other peaks.

In order to investigate the importance of the chain transfer reaction, PBE was substituted, in the photocurable mixture, by PBOH. The results are reported in Table III. They show an increase of the gel content to 98%, indicating that the additive reacts with the growing chains and is linked to the network. Also the final epoxy group conversion increases in the presence of PBOH in the mixture. A similar behavior was observed in the case of the photopolymerization of vinyl ethers in the presence of alcohols [20]. Therefore it is evident that hydroxyl groups interact with the growing chains and impart flexibility to the UV cured films. This reaction increases the final epoxy group conversion due to the higher mobility of the chain. However, the final epoxy group conversion, in the presence of PBOH (Table III) is always lower than the final conversion achieved in the presence of PBE (Table II) and never reaches a complete conversion as in the case of PBE mixtures. We can conclude that PBE is involved in the copolymerization reaction through its epoxy groups.

TABLE III Properties of the UV cured films obtained from DGE-PBOH mixtures

| Sample | Gel content (%) ^a | Conversion (%) ^b |
|------------------------|------------------------------|-----------------------------|
| Pure DGE | 90 | 55.8 |
| DGE:PBOH 90 : 10 wt/wt | 98 | 60.7 |
| DGE:PBOH 80 : 20 wt/wt | 97 | 71.3 |
| DGE:PBOH 50 : 50 wt/wt | 98 | 70.6 |

^aAfter 20 hours of CHCl_3 treatment.

^bEpoxy groups final conversion calculated on the basis of the IR peak at 847 cm^{-1} .

TABLE IV Properties of the UV cured films obtained from CE/PBE and CE/PBOH mixtures

| Sample | Gel content (%) ^a | Conversion (%) ^b |
|-----------------------|------------------------------|-----------------------------|
| Pure CE | 88 | 45.3 |
| CE:PBE 90 : 10 wt/wt | 99 | 65.5 |
| CE:PBE 80 : 20 wt/wt | 98 | 77.3 |
| CE:PBE 70 : 30 wt/wt | 95 | 79.5 |
| CE:PBE 50 : 50 wt/wt | 97 | 99.6 |
| CE:PBOH 90 : 10 wt/wt | 97 | 55.8 |
| CE:PBOH 80 : 20 wt/wt | 98 | 64.9 |
| CE:PBOH 50 : 50 wt/wt | 97 | 72.9 |

^aAfter 20 hours of CHCl_3 treatment.

^bEpoxy groups final conversion calculated on the basis of the IR peak at 795 cm^{-1} .

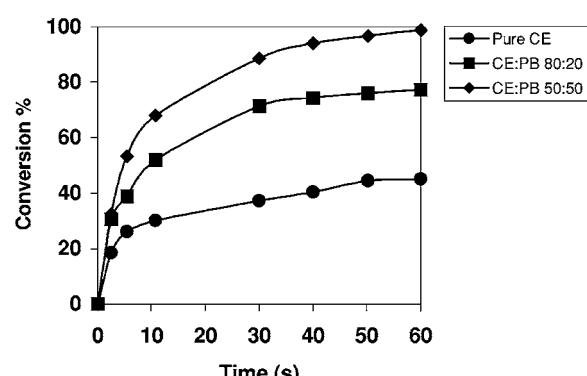


Figure 2 Kinetic curves of Pure CE (●) compared with the mixture CE:PBE 80 : 20 wt/wt (■) and CE:PBE 50 : 50 wt/wt (▲).

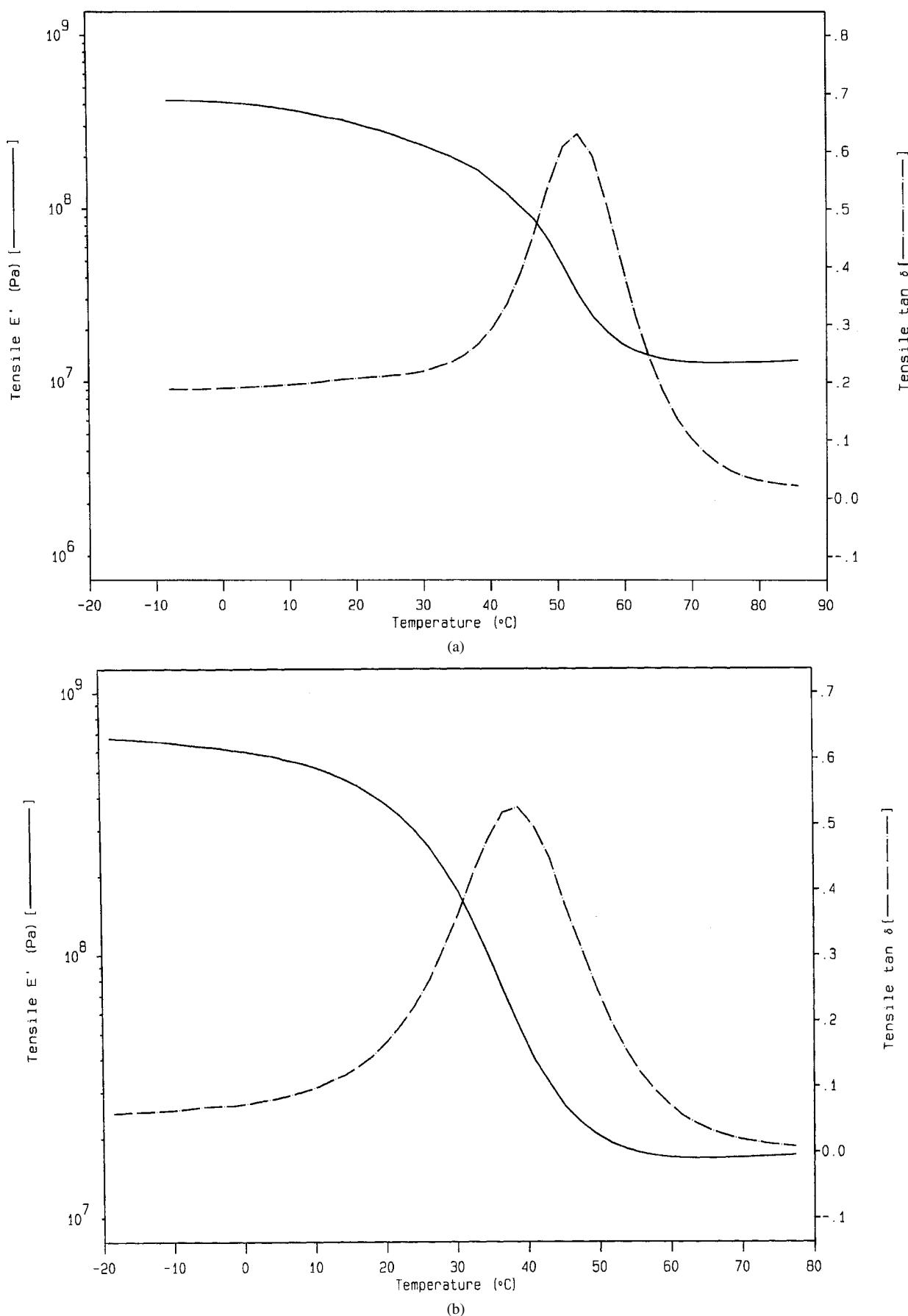


Figure 3 DMTA thermogram of pure DGE UV cured film (A) and of the mixture DGE:PBE 80:20 w/w (B).

In conclusion, we can assume that the PBE additive is incorporated into the polymer network both through a copolymerization reaction involving its epoxy groups and via a chain transfer reaction induced by the presence of the hydroxyl groups. The same experiments were

repeated by using as a monomer a bicycloaliphatic diepoxide (CE), having a different structure and reactivity [19]. In this case the ring opening polymerization proceeds more rapidly upon UV irradiation, but only 45% degree of conversion is achieved due

to the vitrification effect. The results obtained are reported in Table IV and Fig. 2: it is evident that, the final epoxy group conversion increases in the presence of PBE, reaching a complete conversion in the presence of 50 wt% of the additive. The gel content of the UV cured films obtained in the presence of PBE or PBOH additives, show the same behavior as obtained for DGE monomer, confirming the proposed reaction mechanism. We can conclude that also in the case of the biscycloaliphatic epoxide, the PBE additive is incorporated into the polymer network through a copolymerization and a chain transfer reaction.

3.2. Properties of the UV cured films

Thermal and dynamic-mechanical analyses were performed on the UV cured films. While DSC analysis gives information about the thermal behavior, DMTA analysis allows the evaluation of the elastic and viscous component of the modulus of the material in a very large temperature interval. Therefore these techniques allow a complete characterization of the thermal and mechanical properties of the materials.

In Fig. 3 a typical DMTA thermogram of the pure DGE UV cured film is reported and compared with that obtained from a DGE/PBE 80:20 wt% mixture. In the T_g region a strong decrease of E' is evident, while $\tan\delta$ shows a maximum which is assumed as the T_g of the cured films [21]. In Table V the T_g values obtained through DSC and DMTA analyses of the films obtained in the presence of PBE and PBOH are reported. It can be observed that the T_g values obtained by DMTA are higher than those obtained by DSC; similar results were reported previously and attributed to a frequency effect [22].

From the data reported in Table V it is possible to observe that by increasing the amount of PBE and PBOH in the mixture, a decrease of T_g is obtained. We can also observe that the T_g values of the mixtures containing PBE are always higher than those obtained with the mixtures containing PBOH. These results can be attributed to a higher degree of crosslinking of the films

TABLE V T_g values of the UV cured films obtained from CE/PBE and CE/PBOH mixtures

| Sample | | T_g (°C) | |
|----------------------|-------|------------|--|
| Sample | DMTA | DSC | |
| Pure DGE | 53.1 | 37.6 | |
| Pure PBE | 30.0 | 18.3 | |
| DGE:PBE 90:10 wt/wt | 46.7 | 30.5 | |
| DGE:PBE 80:20 wt/wt | 43.3 | 26.3 | |
| DGE:PBE 70:30 wt/wt | 38.9 | 20.2 | |
| DGE:PBE 50:50 wt/wt | 32.2 | 15.6 | |
| DGE:PBOH 90:10 wt/wt | 40.2 | 25.6 | |
| DGE:PBOH 80:20 wt/wt | 38.8 | 21.3 | |
| DGE:PBOH 50:50 wt/wt | 33.2 | 16.5 | |
| Pure CE | 214.3 | 195.8 | |
| CE:PBE 90:10 wt/wt | 200.6 | 188.6 | |
| CE:PBE 80:20 wt/wt | 190.6 | 175.7 | |
| CE:PBE 70:30 wt/wt | 182.2 | 168.3 | |
| CE:PBE 50:50 wt/wt | 172.4 | 155.6 | |
| CE:PBOH 90:10 wt/wt | 202.6 | 187.4 | |
| CE:PBOH 80:20 wt/wt | 184.2 | 170.6 | |
| CE:PBOH 50:50 wt/wt | 171.5 | 153.4 | |

obtained in the presence of PBE, due to the occurrence of the copolymerization reaction.

4. Conclusions

The cationic UV curing of a biscycloaliphatic and a diglycidyl epoxide was investigated in the presence of an epoxy-hydroxy functionalized polybutadiene (PBE). It has been concluded that PBE is incorporated into the polymer network both via a copolymerization reaction of the epoxy groups and via a chain transfer reaction involving hydroxyl groups. Experiments performed in the presence of hydroxy functionalized polybutadiene (PBOH) confirm the suggested mechanism. The investigation of the properties of the cured films shows that, in the presence of PBE and PBOH, the final epoxy groups conversion increases reaching completion with 50/50 w/w mixtures, while the gel content is always near 100%. The T_g values of the cured films decrease sharply in the presence of the additives, confirming the strong flexibilization effect and the interesting possible applications of the obtained coatings.

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