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FLUORINATED HYDROXYTELECHELIC POLYBUTADIENE
AS ADDITIVE IN CATIONIC PHOTOPOLYMERIZATION OF AN EPOXY RESIN

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ABSTRACT
Fluorinated hydroxytelechelic polybutadiene (PBF), synthesized from the radical addition of a
fluorinated mercaptan onto a hydroxytelechelic polybutadiene was used as efficient surface and
mechanical modifiers in original formulations to enable the UV cationic polymerization of a
telechelic diepoxy cycloaliphatic resin, leading to crosslinked films. Various amounts of PBF were
used (ranging between 0 and 15 wt. %). The kinetics of photocrosslinking revealed that the
diepoxyde conversion reached 70 % only in the absence of PBF while it worthed ca. 90 % in the
presence of 10 wt. % of PBF. When the PBF content increased, the dynamic mechanical
measurements showed that: i) the glass transition temperature values decreased, and ii) the
resilience increased. The hydrophobicity of these films was investigated from the water contact
angles (WCA) values showing a surface modification of the epoxy based system. Indeed, great
modifications were noted on the extreme surface (i.e., air side) of the films (with WCA values as
high as 120 °) in contrast to those observed on the substrate side.
1. INTRODUCTION

UV-induced cationic photopolymerization of epoxy monomers is a well-known process and of great interest as a result of its high number of industrial applications\(^1\). The UV-polymerizable formulations are solvent free, the production rates are high and the energy required can be less compared to thermal curing\(^2\). Moreover the cationic photopolymerization of epoxy monomers possesses some distinct advantages such as the lack of inhibition by oxygen, a low shrinkage, good mechanical properties of the UV-cured materials and good adhesion properties of UV-cured films to various substrates\(^3\). Finally, the monomers employed are generally less toxic and less irritant\(^4\) than acrylates and methacrylates extensively used in the radical mechanism. Therefore, extensive work has been carried out to investigate the photocuring of epoxides, focusing mainly on the reaction kinetics and the properties of the cured materials\(^5\)\textsuperscript{--}\textsuperscript{13}. Recently, a study by Fernandez-Francos \textit{et al.}\textsuperscript{14} discussed the influence of the photocuring temperature and the amount of the initiator on the properties of fully cured epoxy material. Other interesting reports showed that certain epoxide monomers display high reactivity in photoinitiated cationic polymerization and are suitable for industrial applications while others undergo apparently slow reactions and are therefore not attractive. Some epoxy monomers that possess basic groups as part of their structures are not polymerizable at all under cationic conditions\(^15\)\textsuperscript{--}\textsuperscript{17}. For this reason, the number of available epoxide monomers that are useful in applications involving photoinitiated cationic polymerization is still limited. Accordingly, most of present and past research emphasis has been placed on developing and optimizing only those monomer-photoinitiator systems that display the highest possible reactivity. One of this monomer is 3,4-epoxycyclohexylmethyl-3’,4’-epoxycyclohexyl carboxylate, which leads to cured polymers characterized by high mechanical properties and solvent resistance, but having a rigid structure. They exhibit rather poor elongation and flexibility characteristics. It is well-known that, in many coatings applications there is a need for toughness and flexibility at the same time ensuring considerable elongation at break. For this reason, it is desirable to find out ways to obtain good mechanical characteristics of UV cured epoxy coatings, together with high flexibility. In the literature, the introduction of reactive plasticizing agents in the UV curable formulations are reported to increase the resilience behavior\(^18\)\textsuperscript{--}\textsuperscript{20}: the presence of a plasticizing agent linked to the epoxy network increases the flexibility and the impact resistance of the cured product giving rise to a good balance of the mechanical properties. Hydroxyl containing additives were investigated with the aim of introducing flexibilization on UV cured networks\(^21\), as the use of alcohols as the chain transfer agents in cationic polymerization was first indicated by Penczek \textit{et al.}\textsuperscript{22}, then confirmed for the UV curing processes by Crivello \textit{et al.}\textsuperscript{23}.
It was shown that in a network forming polymerization, the growing chain end becomes fixed to the immobile three-dimensional network. If the network is glassy, the polymerization is stopped and a large number of oligomers remain trapped into the glassy polymer network. When the chain transfer occurs, new chains carrying reactive species are formed: they are not linked to the network and are, therefore, highly mobile. Higher polymerization rates result from the removal of the restriction to diffusion as well as from a decrease in the average crosslinking density. Also epoxy-hydroxyl functionalized polybutadiene can be incorporated into an epoxy polymeric network, during cationic UV curing of an epoxy formulation, both via a copolymerization reaction of the epoxy groups and via a chain transfer reaction involving hydroxyl groups\textsuperscript{24}. The investigation of the properties of the cured films showed that their $T_g$ decreased sharply in the presence of the hydroxylated additives with an important gain in toughness.

Pursuing these investigations, a fluorinated hydroxytelechelic polybutadiene was synthesized and used as an original additive in cationic UV curing of an epoxy based system. The use of fluorinated monomers or fluorinated alcohols to modify epoxy networks was previously described\textsuperscript{25-27}: peculiar characteristics, connected to the presence of fluorine atoms at the surface, were imparted to the coatings, in particular hydrophobicity and oleophobicity.

The aim of this study is to induce not only surface modification of the epoxy based system by introducing the fluorinated hydroxyl additive, but also to achieve a bulk modification by choosing a rubbery oligomer as a modifier, so that coatings with hydrophobic surface properties and improved network flexibility and resilience can be obtained.

2. EXPERIMENTAL

2.1 Materials

A fluorinated hydroxytelechelic polybutadiene (PBF) was synthesized by radical (various initiators were used such as AIBN, \textit{ditert} butyl peroxide, and t-butyl peroxyprivalate, or photochemically
induced) addition of 1H,1H,2H,2H-perfluorooctyl-1-mercaptan onto hydroxytelechelic polybutadiene (HTPBd, kindly supplied by Atofina) of average molecular weights of 1000 g.mol⁻¹, polydispersity index of 2.5 and functionality of 2.3. The reaction is represented by Scheme 2.

A typical recipe is as follows: in a three necked round bottomed flask equipped with a condenser and a device for a nitrogen flow, was magnetically stirred, under nitrogen, 0.046 g (0.192 mmol) of ter-butyl peroxypivalate, 0.923 g (2.43 mmol) of 1H,1H,2H,2H-perfluorooctyl-1-mercaptan, 10.051 g (9.61 mmol) of HTPBd and 50 mL of THF. After stirring for 7 hrs at 75 °C, the mixture was cooled to room temperature and the solvent evaporated. Then, the modified HTPBd (PBF) was precipitated from methanol twice to allow the unreacted mercaptan to be eliminated (this was checked by the absence of the characteristic triplet centered at 1.50 ppm in the ¹H NMR spectrum, assigned to the SH end-group of the mercaptan) to lead to an orange viscous oil. As previously reported²⁸, ¹H NMR spectroscopy and elemental analyses enabled to assess the grafting percentage (11 %) while the ¹⁹F NMR spectrum confirmed the presence of the perfluorohexyl pendant chain. The fluorine content in the resulting grafted PBF was 28.2 %.

3,4-Epoxycyclohexylmethyl-3’,4’-epoxycyclohexyl carboxylate (CE), UVACURE1500 from CYTEC Company, was employed as a reference epoxy resin. The photoinitiator was a commercially available mixture of antimonate sulfonium salts (UVI 6976) supplied by the Dow Company: it was given as a solution in propylene carbonate (50 % w/w) and it was added into the curable mixtures at a concentration equal to 2% wt/wt. The structures of the monomer and of PBF additive are reported in Scheme 1.

2.2 Preparation of the Samples
The photocurable formulations were prepared by mixing different amounts (ranging between 5-15 wt. %), of the fluorinated hydroxytelechelic polybutadiene (PBF) additive to the epoxy resin, and following adding 2 wt. % of the cationic photoinitiator. The list of formulations is reported in Table 1. The formulations were coated onto a glass slide using a wire-wound applicator. The films were exposed to UV irradiation by using a Fusion lamp (Hg bulb), with radiation intensity on the surface of the sample of 280 mW/cm² and a belt speed of 6 m/min. Fully cured films of about 100 µm thick were obtained.

INSERT TABLE 1

2.3 Techniques of Characterization

The photopolymerization was monitored by Real-Time FT-IR spectroscopy, using a Thermo-Nicolet 5700 instrument. The formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the UV beam, which induced the polymerization, and to the IR beam, which analyzed in-situ the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Epoxy group conversion was monitored by the decrease of the absorbance of the epoxy groups in the region 760-780 cm⁻¹: the absorbance was normalized using the ester band at 1670 cm⁻¹ as an internal reference. A medium pressure mercury lamp equipped with an optical waveguide was used to induce the photopolymerization (light intensity on the surface of the sample of about 30 mW/cm²).

The gel content was determined on the cured films by measuring the weight loss after 24 hours extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

Dynamic mechanical thermal analyses (DMA) were carried out with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration.
Impact resistance measurements were performed with an ATS FAAR Charpy pendulum, according to ASTM D256 method. The fracture surfaces of the samples employed for the impact resistance tests were analyzed by SEM microscopy.

The morphology and the energy dispersive analysis of X-rays of the materials were investigated by Scanning Electron Microscopy (SEM) analysis using LEO (ex LEICA, ex CAMBRIDGE) S260 equipped with a system of microanalysis-X. Accelerating voltage of 300 V to 3 kV (accelerating rate of 100 V) and 4 kV to 30 kV (accelerating rate of 1 kV) was applied. Samples were put into liquid nitrogen to be cryofractured, the cross section was analyzed. Samples were metallized with carbon, under vacuum.

Contact angle measurements were measured with a Krüss DSA10 instrument, equipped with a video camera. Analyses were made at room temperature by means of the sessile drop technique. Five measurements were performed on every sample and the values were averaged. The measuring liquid was double distilled water ($\gamma = 72.1 \text{ mN/m}$).

3. RESULTS AND DISCUSSION

3.1 Photopolymerization of the epoxide in the presence of the fluorinated polybutadiene

The fluorinated polybutadiene (PBF) synthesized by the radical addition of a fluorinated mercaptan onto the double bonds of a hydroxytelechelic polybutadiene (Scheme 2) was employed, as additive, in the cationic UV curing of 3,4-epoxycyclohexylmethyl-3’,4’-epoxycyclohexyl carboxylate (CE). It was added to the epoxy monomer in different amounts as summarized in Table 1. The compatibility of PBF in the CE resin was assessed by visual inspection; the highest concentration insuring homogeneous formulations was about 15 %wt..

The effect of the presence of PBF on the kinetics of the CE photopolymerization was investigated by means of real-time FT-IR. The telechelic diepoxyaliphatic resin is able to polymerize via a cationic photoactivation leading to a crosslinked network, while a chain transfer reaction can take place involving the hydroxyl function of PBF. The conversion curves as a function of irradiation
time for the neat CE resin and in the presence of increasing amounts of PBF, are reported in Figure 1.

INSERT FIGURE 1

While the slope of the curves gives an indication of the rate of polymerization, the plateau value gives the final epoxy group conversion. In agreement with the literature\textsuperscript{15}, the CE resin polymerization proceeded quite rapidly at the beginning and then slowed down markedly when the glassy network was formed (T\textsubscript{g} = 190 °C). As a result, a large amount of epoxy groups remained trapped in the polymer network and could not diffuse further so that the propagation reaction stopped. It was noted that the final conversion is around 70%. When the PBF was added, the initial reaction rate did not change, while an increase of the epoxy group conversion was achieved. In the presence of 10 wt.% of PBF the epoxy group conversion rose to almost 90%.

INSERT SCHEME 3

This behavior is explained on the basis of a chain transfer mechanism involving the hydroxyl groups of PBF, as reported in Scheme 3: the carbocationic growing chain is terminated by reaction with hydroxyl group hence inducing consequent decreases of the chain length and of the crosslink density. The introduction of ether free-dangling ends makes the network more flexible; therefore, the propagation reaction proceeds increasing the conversion. Simultaneously, a proton is produced which can initiate a new polymeric chain. As a consequence of this reaction, the network structure is therefore characterized by a greater flexibility. Hence, the lowering of the glass transition temperature of the cured networks is expected, as it will be discussed further.

The occurrence of the chain transfer reaction and thus, the covalent incorporation of PBF in the network structure, is confirmed by the high value of the gel content also in the presence of a high amount of the additive (always above 96%, see Table 2). These results indicate that the additive is tightly crosslinked into the polymer network and therefore takes part to the growing polymeric chain. In fact, if polybutadiene would not have been part of the crosslinked network, it would have
been extracted giving rise to definitely lower gel content which, on the contrary, is always higher than 96%.

INSERT TABLE 2

3.2 Bulk properties
Dynamic mechanical analyses (DMA) were performed on cured films to evaluate the glass transition temperatures (Tg), defined as the maximum peak of tanδ curves. The values are reported in Table 2. A decrease of Tg values is observed when increasing the amount of PBF in the photocurable formulation, arising from the chain transfer reaction previously explained.

The resilience behavior of the cured samples has been investigated by Charpy measurements. The data, reported in Table 2, show that the resilience increases from 7.53 J/cm² for the pure CE cured resin to 9.55 J/cm² for the cured formulation containing 15 wt. % of PBF. This toughness increase can be attributed both to the flexibilization effect induced by the chain transfer reaction, as indicated by the decrease of the Tg values, as well as to the introduction of polybutadiene in the epoxy matrix. As already observed in a past work \(^{11}\), polybutadiene can segregate and give rise to phase separation. Scanning electron microscopy (SEM) inspections of the cryofracture of the sample containing 15 wt. % PBF showed the formation of polybutadiene domains with an average size of about 50-80 μm (Figure 2).

INSERT FIGURE 2

Energy dispersive X-ray (EDX) analysis (Figure 3) on this area (clear zones) exhibited the expected peaks of carbon and oxygen atoms but also revealed the presence of fluorine atoms of PBF, in contrast to the dark zones that did not show any trace of fluorine.

INSERT FIGURE 3

Examining the picture, a good interaction of the polybutadiene with the surrounding epoxy polymer matrix appears. The interaction between the polybutadiene domains and the polymer network could be the result of the chemical linkage between both the components due to the chain transfer reaction.
3.3 Surface properties

As reported in the experimental section, the formulations having different contents of PBF were used to coat glass slides. Glass slides were coated with mixtures having different contents of PBF. The homogeneous films obtained were peeled off the substrate and the contact angles versus water on both sides of the films have been measured. On the surfaces exposed to air, i.e. the air side of the films, an interesting surface modification as a function of the fluorinated additive concentration was noted. On the contrary, the glass side showed no modification of the surface properties, whatever the amount of the additive. The plot in Figure 4 clearly evidences that PBF is effective only on the air side of the film, where the contact angle versus water increases and overcomes 90 °, meaning that the wettability is reduced and the surface becomes hydrophobic.

On the glass side, the same wettability of the pure pure CE resin, around 70 °, has been observed. This is an important result because it is possible, in this way, to obtain an hydrophobic surface without affecting the good adhesion properties of epoxy coatings onto polar substrates.

The contact angle for the film containing 15 wt. % of PBF is high (120 °) and similar to that exhibited by a fully fluorinated polymer, which are always highly hydrophobic. This high hydrophobicity suggests a surface segregation of the fluorinated groups: due to its low surface energy, PBF can migrate towards the air interface and concentrate at the outermost layer of the cured film. A similar behavior was previously observed for different photocured systems in the presence of fluorinated additives.

This surface segregation was confirmed by EDX measurements taken both from the air surface of the cured samples. EDX analysis of the surface (Figure 5) exhibited a strong peak due to fluorine
atoms whose intensity is higher than the peaks assigned to carbon and oxygen. A negligible amount of fluorine was found on the other surface.

The surface modification was stable and irreversible. The wettability was checked many weeks after film preparation and the contact angle values were unchanged. These interesting results arise from the fact that the additive is covalently linked to the network as it takes part in the polymerization process through a chain transfer reaction.

**INSERT FIGURE 5**

*Acknowledgement:* The authors thanks Nathalie Morcelet for conducting SEM/EDX analyses.

**CONCLUSION**

A fluorinated hydroxytelechelic polybutadiene (PBF) was synthesized and used as an additive in the cationic UV curing of a dicycloaliphatic epoxy resin (CE). An increase of epoxy group conversion was achieved by increasing PBF content in the photocurable formulations. This result was explained on the basis of a chain transfer reaction, involving OH groups, which induces the decrease of the chain-length and crosslinking density, achieving a delay on “glassification” process.

As a consequence, the bulk properties of the films were modified: the glass transition temperature was decreased and the toughness enhanced. A surface modification was also observed in the presence of PBF: selectively the air sides of the films were made hydrophobic. In fact, a surface segregation of the low energy component, the fluorinated polybutadiene, was found by EDX analysis.

In conclusion, the fluorinated hydroxytelechelic polybutadiene showed interesting potentiality as the additive with the possibility to tailor the final properties of the cured films. Highly hydrophobic epoxy coatings endowed with good adhesion and mechanical properties, and improved toughness could thus be achieved.
REFERENCES


SCHEME CAPTIONS

Scheme 1: Chemical Structure of the 3,4-epoxycyclohexylmethyl-3’,4’-epoxycyclohexyl carboxylate (CE) monomer and fluorinated hydroxytelechelic polybutadiene (PBF) additive and weight percentage composition of photocurable formulations.

Scheme 2: Synthetic route for the fluorinated hydroxytelechelic polybutadiene (PBF) by radical (or photochemical) addition of 1H, 1H, 2H, 2H-perfluorooctyl-1-mercaptan onto hydroxytelechelic polybutadiene.

Scheme 3: Chain transfer reaction of 3,4-epoxycyclohexylmethyl-3’,4’-epoxycyclohexyl carboxylate (CE) resin by a generic hydroxyl containing additive.
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TABLE CAPTIONS

Table 1: Composition of the formulations for various coatings

Table 2: Conversion of the epoxy group after 2 minutes of irradiation and bulk properties of the cured films.
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<table>
<thead>
<tr>
<th>Coating type</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE</td>
<td>Pure CE</td>
</tr>
<tr>
<td>PBF-5</td>
<td>CE/PBF 95:5 wt/wt</td>
</tr>
<tr>
<td>PBF-10</td>
<td>CE/PBF 90:10 wt/wt</td>
</tr>
<tr>
<td>PBF-15</td>
<td>CE/PBF 85:15 wt/wt</td>
</tr>
</tbody>
</table>
Table 2: Conversion of the epoxy group after 2 minutes of irradiation and bulk properties of the cured films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Epoxy group conv. (%)</th>
<th>Gel content (%)</th>
<th>Tg (°C)</th>
<th>Resilience (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE</td>
<td>71</td>
<td>97</td>
<td>190</td>
<td>7.53</td>
</tr>
<tr>
<td>PBF-5</td>
<td>80</td>
<td>96</td>
<td>184</td>
<td>8.66</td>
</tr>
<tr>
<td>PBF-10</td>
<td>88</td>
<td>96</td>
<td>180</td>
<td>9.09</td>
</tr>
<tr>
<td>PBF-15</td>
<td>--</td>
<td>95</td>
<td>176</td>
<td>9.55</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Figure 1: Real-time FT-IR kinetic curves of pure CE resin and in the presence of increasing amounts of PBF as the additive

Figure 2: Scanning electron microscopy analysis of fracture surface of PBF-15 UV cured sample

Figure 3: Advancing contact angles for cured films containing various amounts of PFB (on glass (■) and on air (♦) sides)

Figure 4: Energy dispersive X-Ray analysis of PBF-15 cured sample taken from the surface, showing the different elements (C, O, F).

Figure 5: Energy dispersive X-Ray analysis of PBF-15 sample taken from the bulk, showing carbon and oxygen atoms and only traces of fluorine
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