Cross-linked Polyperoxides for Photoremovable Adhesives

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Photoremovability of cross-linked polyperoxides was investigated considering the application to dismantlable adhesives. Applying lap-shear stress on the glass joints bonded by the cross-linked polyperoxides, i.e., the alternating copolymer of 2-hydroxyethyl sorbate and oxygen cross-linked by tolylene 2,4-diisocyanate, resulted in the failure of the glass adherend. UV irradiation on the bonded glass joints more than 19 J/cm² resulted in a significant decrease in the lap-shear adhesion strength due to the photodegradation of the cross-linked polyperoxides, and the bonded glass joints were successfully debonded without breaking the glass adherends. The failure mode was the cohesive failure of the adhesive and the residue of the cross-linked polyperoxides heavily adhered on the both debonded glass adherends. The additional photoirradiation on the debonded glass adherends in tetrahydrofuran resulted in the significant removal of the adhered cross-linked polyperoxide due to the further photodegradation. After 150 J/cm² irradiation, the adhesive residues were completely wiped off from the glass adherends.

Keywords: Cross-linked polymer, Degradable polymer, Polyperoxide, Dismantlable adhesive, Photodegradation

1. Introduction
Cross-linked polymers have superior mechanical and thermal properties and are widely used for adhesives, sealants, coatings, and paints. In the case of adhesives, cross-linked adhesives can achieve much higher bonding strength, thermal and solvent resistances, and durability than non-cross-linked adhesives. However, bonded materials by cross-linked adhesives encounter difficulties in debonding and the removal of the adhesives from adherends. Adhesives exhibiting both good adhesion properties and debondability are called dismantlable adhesives and are attracted much attentions in the view point of material recycling and temporary bonding. Dismantlable adhesives including pressure–sensitive adhesives based on various debonding mechanisms are reported [1-14]. Cross-linked polymers containing degradable groups such as tertiary esters and tertiary carbonates [15-17], Diels-Alder adduct moieties [18,19], acetal group [20], disulfide bond [21-23], and peroxo bond [24-27] are one class of candidates for dismantlable adhesives.

We have reported dismantlable adhesives using polyperoxides [2,6,13,28], which contain peroxy bonds as a repeating unit of the main-chain (Scheme 1). Although oxygen acts as inhibitor in the radical polymerization of vinyl monomers, radical alternating copolymerization of 1,3-dienes such as sorbic esters with oxygen smoothly proceed and yield polyperoxides in a good yield [27,29,30]. Various polyperoxides including cross-linked polyperoxides [24-26], block and graft copolymers containing polyperoxide segments [6,31], core-shell type

Scheme 1. Structure of polyperoxide from sorbic esters.
particles encapsulating polyperoxides [28] were also successfully synthesized. Polyperoxides undergo main-chain degradation by various stimuli, i.e., thermal degradation, photodegradation, redox degradation, and enzymatic degradation [30,32]. However, undesired side-reactions such as hydrogen abstraction by an oxygen-centered radical and the subsequent carbon-carbon bond formation take place and non-degradable network polymers are generated, especially in bulk at higher temperature. When cross-linked polyperoxides are applied to dismantlable adhesives, the undesired cross-linking as side reactions of polyperoxides prevent dismantling. Furthermore, the undesired cross-linking causes difficulties in the removal of the adhesive residues on adherends after dismantling. Considering practical applications, removal of adhesive residues from adherends is important issue. In this study, photodegradation of cross-linked polyperoxides and application to photoremovable adhesive materials are investigated with expectation that the aforementioned undesired side reactions would be suppressed under the conditions of photodegradation at room temperature.

2. Experimental

2.1. Materials

2-Hydroxyethyl sorbate (HES) was synthesized according to the methods described in the literature from sorbic acid and ethylene glycol using $N,N'$-dicyclohexylcarbodiimide in the presence of 4-(dimethylamino)pyridine [26]. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) (Wako Pure Chemical Industries, Ltd., Japan) was recrystallized from methanol. The polyperoxide from HES with oxygen (PP-HES) ($M_\text{n} = 2,800-3,500$, $M_\text{w}/M_\text{n} = 1.7-1.9$), were prepared by the radical alternating copolymerization of HES with oxygen initiated by AMVN in 1,2-dichloroethane at 30 ºC for 6 h based on the literature [26]. Formation of the alternating copolymer of HES and oxygen was confirmed by $^1$H NMR spectroscopy. Sorbic acid (Kishida Chemical Co., Ltd. >98.5%), ethylene glycol (Wako Pure Chemical Industries, Ltd., Japan >99.0 %), $N,N'$-dicyclohexylcarbodiimide (Wako Pure Chemical Industries, Ltd., Japan, >95.0%), 4-(dimethylamino)pyridine (Wako Pure Chemical Industries, Ltd., Japan, >99.0%), and tolylene 2,4-diisocyanate (TDI) (Tokyo Kasei Kogyo, Ltd., Japan, >98.0%) were used as received. Other reagents and solvents were used without further purification or purified according to conventional methods.

2.2. Measurements

The number- and weight-average molecular weights ($M_\text{n}$ and $M_\text{w}$) were determined by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. The $^1$H NMR spectra were recorded using a Bruker AN300N (300 MHz) spectrometer. UV absorption spectrum was recorded on a SHIMADZU UV-2400.

2.3. Lap-shear adhesion tests

The lap-shear adhesion tests were performed according to “ASTM D1002, standard test method for apparent shear strength of single-lap-joint adhesively bonded metal specimens by tension loading (Metal-to-Metal)” using a SHIMADZU universal testing machine AGS-X, with a 1 kN (at maximum) load cell with 1 mm/mim at room temperature. The polyperoxide-based adhesive materials were applied to a surface of the specimen and were treated under the conditions described below. Glass (10 × 70 × 1 mm) was cleaned by ultrasonication in acetone for 15 min and in 2-propanol for 15 min. The adhered area was fixed at 100 mm$^2$ (10 × 10 mm). The average value of three measurements was typically recorded.

To 0.1 mL of acetone, PP-HES (30 mg, 1.6 × $10^{-4}$ mol of OH group) and TDI (14 mg, 8.0 × $10^{-5}$ mol) were added. The mixture was applied on the glass plate, and acetone was removed under vacuo in the dark for 1 h. After removing acetone, the matching surfaces were pressed together. The clamped specimen was kept at 30 ºC under vacuo for 12 h in the dark for the reaction of PP-HES and TDI.

2.4. Photodegradation

Photoirradiation on adhesive residues on adherends was carried out in THF by using a low pressure mercury lamp (Filgen UV253). The adherends with cross-linked PP-HES were placed polymer side up in THF bath at a distance of 3 cm from the light source. The light intensity was measured by a laser power meter (NEOARK, PM-33A) and the light intensity was 5.2
Photoirradiation on lap-shear test joints was carried out under atmospheric conditions using a high pressure mercury lamp (Moritex MSU-6) with a heat-absorbing filter, UVF350, in order to avoid temperature rise during photoirradiation. Lap-shear test joints were placed at a distance of 10 cm from the light source and irradiation was carried out from one side. The light intensity was measured by a UV power meter (USHIO, UIT-101) equipped with a UVD-365PD optical receiver (330-390 nm), and the light intensity was 21 mW/cm².

3. Results and discussion

3.1. Photodegradation of cross-linked PP-HES

UV spectrum of 0.02 wt% PP-HES in THF (peroxy unit in PP-HES = 9.5 x 10⁻⁴ mol/L) is shown in Fig. 1. PP-HES showed absorption at UV region due to a peroxy bond. It is reported that polyperoxides undergo photodegradation by UV irradiation [33]. The thin layer of cross-linked PP-HES on an aluminum plate was soaked in THF for 10 h (Fig. 2(a)). Cross-linked PP-HES was partially solubilized in THF and/or peeled off from the aluminum plate but still significant amount of the cross-linked PP-HES was adhered on the aluminum plate. Photoirradiation by a low pressure mercury lamp from a distance of 8 cm during a soaking in THF resulted in more significant removal of cross-linked PP-HES (Fig. 2(b)). These results clearly show that UV irradiation is effective to solubilize cross-linked PP-HES in THF by photodegradation.

3.2. Photoremovable adhesives based on cross-linked PP-HES

Acetone solution of PP-HES containing TDI was applied on the glass plates in such a way that ca. 10 mg of solutes was on the glass and the cross-linking reaction between the hydroxy groups in PP-HES and the isocyanate groups in TDI was conducted at 30 ºC for 12 h under vacuo. In order to evaluate the effect of the photodegradation of cross-linked PP-HES on lap-shear adhesion strengths, the bonded joints were subjected to photoirradiation by a high pressure mercury lamp for 1.3, 19, 38, and 230 J/cm², where heat-absorbing filter was mounted on the right source and a temperature rise during photoirradiation was negligible. The lap-shear adhesion tests of the bonded joints were performed at room temperature and the results are summarized in Table 1. The joint bonded by cross-linked PP-HES resulted in the material failure of the glass before photoirradiation, and the result is as same as our previous report [2]. Photoirradiation for 1.3 J/cm² brought about the same result as the unirradiated one, i.e., the

![UV spectrum of 0.02 wt% PP-HES in THF.](image)

![Photographs of aluminum plates with cross-linked PP-HES after soaking in THF for 10 h (a) without and (b) with photoirradiation by a low pressure mercury lamp.](image)

Table 1. Results of lap-shear adhesion tests of glass plates bonded by cross-linked PP-HES after photoirradiation.

<table>
<thead>
<tr>
<th>Quantity of light (J/cm²)</th>
<th>Lap-shear strength (MPa)</th>
<th>Failure mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>glass failure</td>
<td>-</td>
</tr>
<tr>
<td>1.3</td>
<td>glass failure</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>2.1^c</td>
<td>cohesive failure</td>
</tr>
<tr>
<td>38</td>
<td>1.2 ± 0.1^c</td>
<td>cohesive failure</td>
</tr>
<tr>
<td>230</td>
<td>1.3 ± 0.3</td>
<td>cohesive failure</td>
</tr>
</tbody>
</table>

^aPhotoirradiation was carried out with a high pressure mercury lamp at room temperature. ^bGlass plate was broken before debonding. ^cResult of a single test.
material failure of the glass because of only slight degradation of cross-linked PP-HES. Photoirradiation for 19 J/cm² resulted in the failure at the cross-linked PP-HES layer without damaging the glass plate, and the lap-shear adhesion strength was 2.1 MPa. After 38 J/cm² irradiation, further decrease in the lap-shear adhesion strength to 1.2 ± 0.1 MPa was observed. Further decrease in the lap-shear adhesion strength was not observed even after 230 J/cm² photoirradiation. In all cases, the failure mode was a cohesive failure. The representative lap-shear adhesion strength-displacement curves are shown in Fig. 3. The lap-shear test joint after 19 J/cm² photoirradiation resulted in a larger displacement and lower strength than the unirradiated test joint due to the progress of the photodegradation of cross-linked PP-HES to decrease its modulus. With increasing the UV exposure to 38 J/cm², the lap-shear strength further decreased as already mentioned.

The surfaces of the debonded glass plates after photoirradiation of 38 J/cm² are shown in Fig. 4(a). As mentioned above, a cohesive failure was observed and cross-linked PP-HES heavy adhered on the both debonded glass plates, i.e., glass plates located at the closer side to the light source (glass A) and the opposite side (glass B) during photoirradiation on the bonded lap-shear test joint. The debonded glass strips were soaked in THF and subsequently subjected to photoirradiation by a low pressure mercury lamp to remove cross-linked PP-HES residue on the glasses. The photographs of the surface after photoirradiation of 56, 94, and 150 J/cm² are shown in Figs. 4(b)-(d). With increasing UV exposure, the amount of adhesive residues on both glass A and glass B decreased and irradiation of 150 J/cm² resulted in significant removal of cross-linked PP-HES from the glass plates. After 150 J/cm² photoirradiation, the glasses were dismantling process of the bonded lap-shear test joint.

![Fig. 3. Representative lap-shear strength-displacement curves of glass specimens bonded by cross-linked PP-HES before (—) and after photoirradiation for 19 (— —), 38 (••••), and 230 J/cm² (— —). The cross mark and arrows indicate the breaking point of the glass plate and debonding point of the bonded joints, respectively.](image)
slightly remained adhesive residues were readily wiped off and clean glass adherends were recovered (Fig. 4(e)).

4. Conclusion

Applications of cross-linked PP-HES to photoremovable adhesives were investigated. The glass adherends bonded by cross-linked PP-HES were successfully debonded by photoirradiation without damaging the adherends, whereas non-irradiated bonded joints brought about breaking of the glass adherends. The residues of cross-linked PP-HES on glass adherends were successfully removed by photoirradiation in THF and a simple wiping.

References