ARTICLE

Cohesive Force Change Induced by Polyperoxide Degradation for Application to Dismantlable Adhesion

Eriko Sato,* Hiroshi Tamura, and Akikazu Matsumoto

Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

ABSTRACT Polyperoxides containing peroxy bonds as the main-chain repeating units are a new class of degradable polymers because of significant changes in their molecular weight and physical properties during a degradation process. In this study, the application of linear and network polyperoxides to dismantlable adhesion was investigated. When the linear polyperoxide obtained from methyl sorbate and oxygen (PP-MS) was used as a pressure-sensitive adhesive (PSA), its shear holding power and 180° peel strength immediately decreased upon heating at 70 °C or under UV irradiation. Low-molecular-weight products, which were generated by the degradation of PP-MS, behaved as a plasticizer to effectively reduce the cohesive force. The adhesive properties of two types of polyperoxides-based network polymers, the cross-linking point and main-chain degradable network polymers, were evaluated. A cross-linking point degradable network polymer was produced by the oxygen cross-linking of dienyl-functionalized poly(ethylene glycol). A main-chain degradable network polymer was formed by the diisocyanate cross-linking of a hydroxy-functionalized polyperoxide. Both network polymers showed a higher adhesive strength than PP-MS due to their three-dimensional network structure. Noteworthy, the adhesive strength of the main-chain degradable network polymer was varied from the level of PSA to structural adhesives by increasing the added amount of the diisocyanate cross-linker. After heating at 110 °C, the cohesive and adhesive strengths significantly decreased. The linear and network polyperoxides are shown to be promising materials for dismantlable adhesion.

KEYWORDS: degradable polymer • network polymer • dismantlable adhesion • cohesive properties • chain degradation

INTRODUCTION

Adhesive strength strongly depends on the properties of the adherend surface, such as wettability and roughness. The chemical and physical treatments of adherend surfaces, such as annealing and plasma treatment, are widely used in order to modify the adhesion properties of the substrates (1−5). Adhesives consisting of polymer materials can also be treated after adhering. For example, post curing affects not only the cohesive force, but also the adhesive strength, i.e., surface interaction between the adhesive and adherend. The degradation of adhesives during use under various conditions, such as exposure to sunlight, moisture, and an oxidative atmosphere, is usually identified as an unfavorable deterioration.

The degradation of polymers accompanies changes in not only their molecular weight and chemical structure, but also their physical and mechanical properties. There are two types of positive applications of degradable polymers. One directly utilizes the degradability, i.e., biodegradable containers and absorbable surgical materials (6, 7). The other utilizes the secondary effect of degradation, i.e., a structural change caused by degradation that further induces another change in the properties of the materials. For instance, positive resist materials use the increased solubility of a degraded polymer to obtain a patterned surface (8). The degradation of polymers also changes their viscoelasticity, rigidity, and polarity, which affect the polymer-to-polymer and polymer-to-substrate interactions. The adhesion strength is sensitive to changes in the cohesive force and interaction between an adhesive layer and substrates (9). Degradable polymers are the one of the best candidates as dismantlable adhesives because their degradability and changes in their properties induced by the degradation are tunable. Beside degradable polymers, several materials based on different strategies have been studied as adhesives that change their adhesion properties corresponding to thermal stimulation. For instance, the reversible Diels−Alder reaction, shape memory polymers, and morphology change of a hot-melt polymer were used as a key reaction or material to reversibly change the adhesive properties (10−13). In general, the polymers used for dismantlable adhesives are required to response to external stimuli that do not deteriorate the adhered materials.

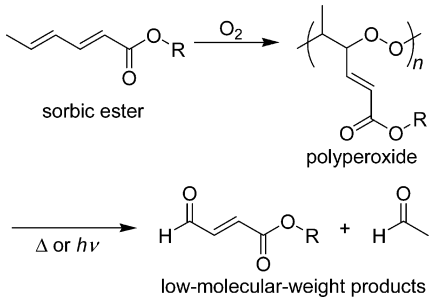
Polyperoxides have been classified into a new type of degradable polymer due to their characteristic degradation via the radical chain mechanism. In the other words, the polyperoxides can change their properties in response to many stimuli over a short time period. We previously reported that the polyperoxides are synthesized by the radical alternating copolymerization of 1,3-diene monomers with oxygen (14, 15). It was revealed that sorbic esters underwent a regiospecific 5,4-propagation and the resulting polyperoxides readily degraded by homolysis of the peroxy bond followed by β-scission to form low-molecular-weight

* Corresponding author. E-mail: sato@a-chem.eng.osaka-cu.ac.jp.
Received for review May 19, 2010 and accepted July 29, 2010

DOI: 10.1021/am1004392

Published on Web 08/16/2010

Scheme 1



degradation products (Scheme 1) (15−17). Various functional polyperoxides, such as water-soluble, cross-linkable, and reactive polyperoxides, were synthesized by the introduction of a functional group into the 1,3-diene monomers (16, 18, 19). We also reported the facile synthesis of dienyl-functionalized precursor polymers using so-called dienylation agents (20, 21). Dienyl-functionalized precursor polymers including telechelic type polymers undergo oxygen cross-linking. In this case, the cross-linking point degradable network polymers are formed. The polyperoxides containing hydroxy groups, such as the polyperoxide from 2-hydroxyethyl sorbate (HES), undergo cross-linking by bifunctional isocyanates, and main-chain degradable network polymers are formed (21). Because of a facile synthetic route, the polyperoxides have started to attract much attention as functional materials, and we have extensively studied application of the polyperoxides in the field of morphology control, drug delivery systems, etc. (22−24).

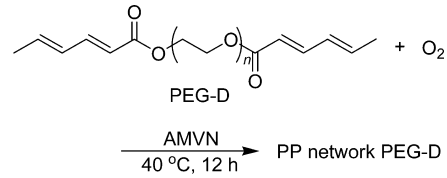
In this study, the adhesion behavior and dismantlability of polyperoxides were investigated using several adhesion tests, such as shear holding power, lap-shear strength, and 180° peel strength measurements. Three types of polyperoxides, i.e., linear, cross-linking point degradable, and main-chain degradable network polyperoxides, were examined as dismantlable adhesives. The effect of the degradation on the adhesion strength, i.e., a cohesive force and an interaction between the polyperoxide adhesive layer and the substrate surface is discussed.

EXPERIMENTAL SECTION

Materials. 2-Hydroxyethyl sorbate (HES) (21) and diene-terminated telechelic poly(ethylene glycol) (PEG-D) (M_n = 1100) (20) were prepared according to the methods described in the literature. Methyl sorbate (MS) was distilled under reduced pressure. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) was recrystallized from methanol. The polyperoxides, PP-MS (M_n = 3100, M_w/M_n = 1.7) and PP-HES (M_n = 4600, M_w/M_n = 1.7), were prepared by the radical alternating copolymerization of sorbic esters (MS and HES) with oxygen initiated by AMVN in 1,2-dichloroethane at 30 °C (15, 21). Tolylene 2,4-diisocyanate (TCI, >98.0%) was used as received. All other commercial chemicals were used as received without further purification.

Measurements. The number- and weight-average molecular weights (M_n and M_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 NMR spectra were recorded using a Bruker AN300N spectrometer. The thermogravimetric and differential thermal analyses (TG/DTA) were performed using a Seiko EXSTAR6000 at the heating rate of 10 °C/min in a nitrogen stream at the flow rate of 30 mL/min. The differential scanning calorimetric (DSC) analysis was performed using a Seiko EXSTAR6000 at the heating rate of 10 °C/min.

Scheme 2



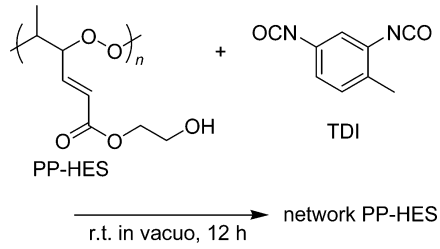
The adhesion tests were performed according to "ASTM D1002, standard test method for apparent shear strength of single-lap-joint adhesively bonded metal specimens by tension loading (metal-to-metal)", "ASTM D3654, standard test methods for shear adhesion of pressure-sensitive tapes", and "ASTM D3330, standard test method for peel adhesion of pressure-sensitive tape" methods, using a Tokyo Testing Machine (TTM) universal testing machine, LSC-1/30, with a 1 kN (at maximum) load cell and MSC-10/500, with a 10 kN (at maximum) load cell. The polyperoxide-based adhesive materials were applied to a surface of the specimen and were treated under the conditions described below. Glass (26.0 × 76.0 × 1.0 mm^3) and nonblasted aluminum (25.0 × 100.0 × 1.5 mm^3) plates were used as the rigid specimens. The adhered area was fixed at 325 mm^2 (12.5 × 26.0 mm^2 for glass and 13.0 × 25.0 mm^2 for aluminum). Specimens were cleaned by ultrasonication in acetone for 15 min and in 2-propanol for 15 min. A PET film (50 μm thickness) was used for the 180° peel test. All the adhesion tests were performed at 25 °C. The average value of three measurements was used.

Preparation of Joint Bonded by PP-MS. Typically, PP-MS (100 mg) was dissolved in chloroform (0.2−0.3 mL), and then applied on the specimen. The specimen was dried in vacuo for 3 h in the dark, and the mating surfaces were pressed together. The specimen was clamped and kept at room temperature for 3 h in the dark.

Preparation of Joint Bonded by PP-network PEG-D. Typically, to PEG-D (200 mg, 2.0 × 10^{-4} mol) in the vessel, which was degassed and charged with oxygen three times, AMVN (12 mg, 4.0 × 10^{-5} mol) was added and mixed. If necessary, the mixture was hand warmed to soften it. The mixture was applied on the specimen, then the mating surfaces were pressed together. The specimen was clamped and heated at 40 °C under an oxygen atmosphere in the dark for 12 h for the reaction of PEG-D and oxygen to form the PP-network PEG-D (Scheme 2).

Preparation of Joint Bonded by Network PEG-D. Typically, to PEG-D (200 mg, 2.0 × 10^{-4} mol) in the vessel, which was degassed and charged with nitrogen three times, AMVN (12 mg, 4.0 × 10^{-5} mol) was added and mixed. If

Scheme 3



necessary, the mixture was hand warmed to soften it. The mixture was applied on the specimen, then the mating surfaces were pressed together. The specimen was clamped and heated at 40 °C under a nitrogen atmosphere in the dark for 12 h to form the network PEG-D without peroxy bonds.

Preparation of Joint Bonded by Network PP-HES. Typically, to 0.2−0.3 mL of acetone, PP-HES (200 mg, 1.06×10^{-3} mol of OH group), and TDI (184 mg, 1.06×10^{-3} mol) were added. The mixture was applied on the specimen, then acetone was removed under vacuo in the dark for 1 h. The application and drying process was repeated 3−5 times and the mating surfaces were then pressed together. The specimen was clamped and kept at room temperature under vacuo for 12 h in the dark for the reaction of PP-HES and TDI to form the network PP-HES (Scheme 3).

Thermal Treatment and UV Irradiation of Test Joint. For the thermal treatment, the test joint without a clamp was placed in a preheated oven. After a predetermined time, the joint was removed from the oven and was naturally cooled to room temperature. For the UV irradiation, a test joint without a clamp was placed at a distance of 10 cm from the UV source (Moritex MUV-250U-L, 500 W) at room temperature.

RESULTS AND DISCUSSION

Linear Polyperoxide as Pressure-Sensitive Adhesives. The representative lap-shear strength-displacement curve of a glass joint bonded by PP-MS showed the typical behavior of pressure-sensitive adhesives (PSAs), i.e., a steep rise in the lap-shear strength followed by a gradual decrease due to stringing was observed (Figure 1). The average of the lap-shear strength was 13.5 ± 4.0 kN/m^2. The value of the lap-shear strength ranged between those of office tape (= 35−70 kN/m^2) and a sticky note (= 0 kN/m^2) (25). After heating the joint at 110 °C for 2 h, the lap-shear strength

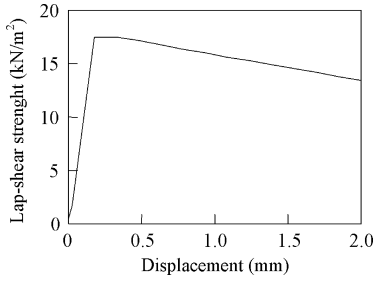


FIGURE 1. Representative lap-shear strength-displacement curve of glass joint bonded by PP-MS.

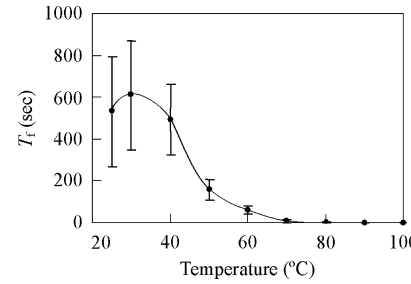


FIGURE 2. Shear holding power of glass joint bonded by PP-MS after heating at each temperature for 1 h.

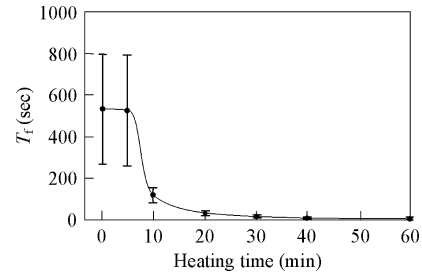


FIGURE 3. Shear holding power of glass joint bonded by PP-MS after heating at 70 °C.

could not be determined due to too weak an adhesion strength (26). In order to investigate the detailed change in the adhesion strength after heating, the shear holding power test was carried out. The time to failure (T_f) against 100 g of weight was determined at each temperature after heating for 60 min (Figure 2). No decrease in the T_f value was observed by heating to 40 °C. The heating at 30 °C resulted in a higher T_f value than the one without heating. It is expected that contact between the PP-MS and substrate was improved due to the improved diffusion of the PP-MS during the heating (27). Above 40 °C, the T_f values significantly decreased and were less than 10 s after heating at 70 °C. The decreases in the T_f value can be attributed to the thermal degradation of PP-MS in addition to the plasticizing effect of the degradation product as described later. The effect of the heating time at 70 °C was also investigated (Figure 3). The T_f value was rapidly decreased after an induction period of ca. 5 min. The induction period is due to the low heat conduction of PP-MS during the thermal treatment. The onset temperature of decomposition (T_{init}) of PP-MS was 114 °C (15), which was determined by a TG analysis at the heating rate of 10 °C/min. The T_{init} value of PP-MS is much higher than the temperature in which a significant reduction in the shear holding power was observed (50−100 °C). The changes in the weight loss of PP-MS, M_n and M_w/M_n, and T_g values after heating at 70 °C are summarized in Table 1. The weight loss was 1.5% after 10 min and 6.6% even after 60 min of heating. The decrease in the M_n value was low (25% reduction after a 30-min heating relative to the initial value). These results suggest that most of the polymer chains still exist without degradation after heating at 70 °C. In our early work, it was reported that when one peroxy bond of the polyperoxides undergoes homolysis, the resulting oxygen-centered radicals undergo further successive β-fragmentation forming low-molecular-weight degradation products (15, 28). It is considered that the degradation products act

Table 1. Property Changes of PP-MS after Heating at 70°C

time (min)	weight loss (wt %)	M_n	M_w/M_n	T_g (°C)
0	0	3100	1.71	−13
10	1.5	2800	1.68	[a]
30	3.9	2300	1.67	[a]
60	6.6	[a]	[a]	−27

[a] Not determined.

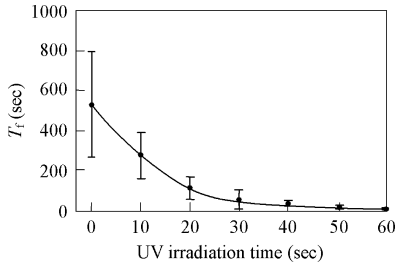


FIGURE 4. Shear holding power of glass joint bonded by PP-MS after UV irradiation at room temperature.

as a plasticizer and the degradation of a small number of chains resulted in an effective decrease in the shear holding power. In fact, the T_g value decreased from −13 to −27 °C after heating at 70 °C for 60 min.

To clarify the durability of PP-MS, the test specimen was kept at 25 °C for 7 days then the shear holding power measurement was carried out. The values of T_f and M_n decreased from 530 ± 260 to 130 ± 30 s and 3100 to 2700, respectively. This result shows that the degradation of PP-MS gradually proceeds even at room temperature and the shear holding power deteriorates. The values of T_f and M_n after 7 days are close to those after 10−20 min at 70 °C. This fact suggests that the shear holding power is affected by the extent of the degradation of PP-MS and not by the degradation conditions. Considering that the shear holding power of PP-MS is reduced under mild conditions, PP-MS is suitable for mild application such as rework processes and temporary bonding and not for adhesives requiring a long stability.

In general, the peroxy bond is labile to UV irradiation (29), and we reported that the degradation of the polyperoxides occurs due to UV irradiation (28). The effect of the UV irradiation on the shear holding power was also investigated (Figure 4). Contrary to the thermal treatment results, the T_f values started to decrease just after the UV irradiation and the shear holding power was almost lost in 60 s. The shear holding power was reduced much faster by the UV irradiation than heating under the conditions used in this study. Although the UV light intensity used in this study is much stronger than that of sunlight, it is expected that a gradual decrease in the shear holding power occurs when PP-MS is applied on a transparent substrate and exposed to sunlight.

As already mentioned, PP-MS behaved like PSAs. To evaluate the peel strength, the 180° peel test was carried out. Although the peel rate was relatively low (30 mm/min) (30), the typical stick−slip failure (27, 31) was observed before the thermal treatment (Figures 5a and 6a). The T_g value of PP-MS was −13 °C, being higher than those for the

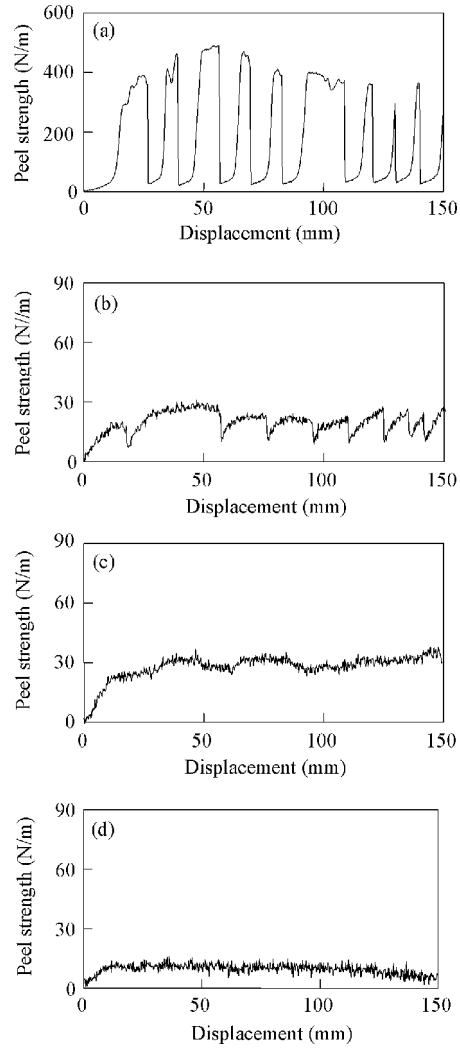


FIGURE 5. Representative peel strength-displacement curves of the test specimen during the 180° peel test bonded by PP-MS (a) before and after heating at 70 °C for (b) 10, (c) 20, and (d) 60 min.

common PSAs (25, 32), and stick−slip failure was occurred. After 10 min of heating at 70 °C, the peel strength obviously decreased and the stick−slip failure was still observed (Figure 5b). Stick−slip failure was no longer observed after 20 min of heating, (Figure 5c), whereas a further decrease in the peel strength was observed after 60 min of heating (Figures 5d and 6b). In all cases, cohesive failure was observed. These results clearly showed that the cohesive force decreased with the increasing heating time, in other words, with the increasing amount of low-molecular-weight products as a plasticizer. The value of the 180° peel strength strongly depends on the experimental conditions such as the peeling rate, therefore the value of the 180° peel strength of PP-MS was compared to that of commercially available office tape measured under the same conditions. The office tape resulted in an ca. 200 N/m 180° peel strength at the peeling rate of 30 mm/min. Although stick−slip failure was observed, before heating, the maximum 180° peel strength of PP-MS was more than twice that of the office tape. After heating at 70 °C for 60 min, the value of the 180° peel strength decreased to less than one-tenth that of office tape. It can be concluded that the changes in the adhesive strength

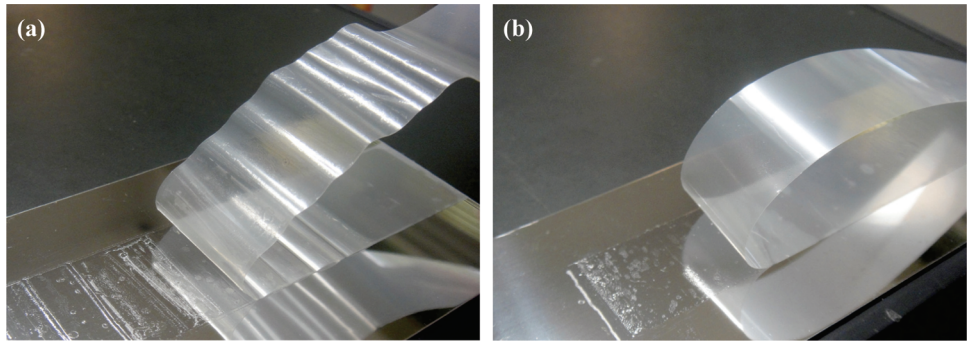


FIGURE 6. Test specimens after 180° peel test (a) before and (b) after heating at 70 °C for 60 min.

caused by the thermal degradation of PP-MS is significant when considering practical applications.

Cross-Linking Point Degradable Network Polyperoxides. Polyperoxide-based network polymers are expected to show a higher cohesive force than the linear polyperoxides, such as PP-MS. We previously reported that precursor polymers having more than two dienyl groups per chain, i.e., the dienyl-functionalized precursor polymer, are cross-linked by oxygen in a solution in the presence of a radical initiator (20, 33). Dienyl-functionalized precursor polymers are also expected to undergo cross-linking by oxygen in bulk and can be used as curable adhesives. The telechelic type dienyl-functionalized poly(ethylene glycol) (PEG-D) with the M_n of 1100 was used as a precursor polymer because low-molecular-weight PEGs showed a good processability in a nonsolvent process (Scheme 2). After the oxygen cross-linking in bulk, the gel, which is insoluble in chloroform, was obtained in 18 wt % yield. The TG/DTA analysis of the isolated gel showed the presence of peroxy bonds, i.e., an exothermic heat evolution was observed and the T_{init} value was determined to be 80 °C by DTA (see the Supporting Information). Contrary to that of PP-MS, a marked weight loss did not occur with heat evolution because the degradation product was mainly nonvolatile poly(ethylene glycol) (20).

The lap-shear strengths of glass and aluminum joints bonded by the PP-network PEG-D were measured. The failure mode of both joints was a combination of adhesive and cohesive failures (see the Supporting Information). The representative lap-shear strength-displacement curves and the average values of the lap-shear strength are shown in Figure 7 and Table 2, respectively. The value of the lap-shear strength was higher than that of PP-MS. The results can be attributed to an increase in the cohesive force becaue of the three-dimensional network formation. The aluminum joint resulted in a higher lap-shear strength than the glass joint. These results suggested that the PP-network PEG-D exhibits a stronger adhesion force on aluminum. After heating the joints at 110 °C for 2 h, the lap-shear strength value decreased. The failure mode was again the combination of adhesive and cohesive failures (see the Supporting Information). It is clear that the cohesive force decreases by the degradation of the peroxy bond at the cross-linking point. Interestingly, the lap-shear strength of the aluminum joint

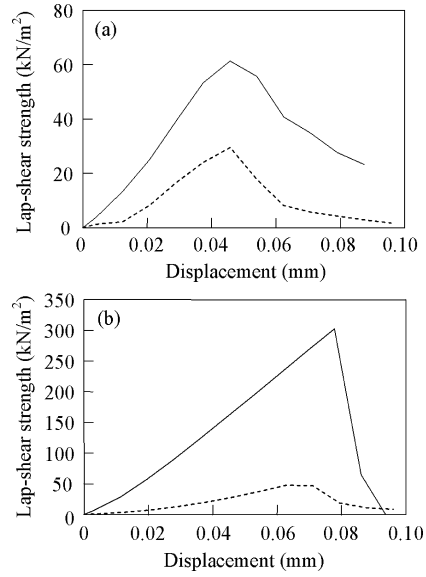


FIGURE 7. Representative lap-shear strength-displacement curves of (a) glass and (b) aluminum joints bonded by PP-network PEG-D before (—) and after (---) heating at 110 °C for 2 h.

Table 2. Results of Lap-Shear Strength Test

network polymer	strip	lap-shear strength (kN/m²) before heating	lap-shear strength (kN/m²) after heating[a]	relative lap-shear strength[b]
PP-network PEG-D	glass	67.4 ± 5.2	32.0 ± 2.2	0.47
	aluminum	276.9 ± 22.5	44.9 ± 3.7	0.16
network PEG-D	glass	58.5 ± 18.8	125.8 ± 23.7	2.15

[a] At 110 °C for 2 h. [b] The value obtained after heating at 110 °C for 2 h relative to that before heating.

decreased to as low as that of the glass joint, i.e., the extent of the decrease was more pronounced on the aluminum joint.

As a control experiment, PEG-D was reacted in the absence of oxygen, and the lap-shear strength was measured. Dienyl compounds undergo radical homopolymerization in the absence of oxygen (14) and the network PEG-D having a nondegradable carbon-to-carbon bond at the cross-linking point is formed. After heating, the lap-shear strength increased by a factor of about two (Table 2). It was expected that the remaining dienyl groups in PEG-D further reacted to form additional cross-linking points during the heating. The newly formed cross-linking point causes an increase in the lap-shear strength. As described later, the reaction of the

Table 3. Effect of Heating Conditions on the Results of the Lap-Shear Strength Test of Glass Specimen Bonded by PP-Network PEG-D

temperature (°C)	time (h)	lap-shear strength (kN/m^2)	relative lap-shear strength[a]
[b]	[b]	67.4 ± 5.2	1.00
80	0.5	70.2 ± 9.2	1.04
80	1	62.2 ± 17.2	0.92
80	2	91.7 ± 13.8	1.36
110	0.5	70.2 ± 15.4	1.04
110	1	47.7 ± 19.7	0.71
110	2	32.0 ± 2.2	0.48

[a] The value obtained after heating relative to that before heating. [b] Specimen before heating.

remaining dienyl groups also competes with the thermal degradation of the peroxy bond. It should be mentioned that the network PEG-D showed a lap-shear strength value as high as that of the PP-network PEG-D before heating. This fact suggests that the lap-shear strength is mainly controlled by the nature of the precursor polymer and the chemical structure of the cross-linking point has a negligible effect. This means that the properties of the adhesives are adjustable based on the choice of the precursor polymers.

The dependence of the lap-shear strength on the heating conditions was investigated in detail (Table 3). Heating at 80 °C resulted in an increase in the lap-shear strength values with the increasing heating time. At 110 °C, a similar increase was observed after 0.5 h and a gradual decrease was observed after 1 h. These results suggest that the frequency of the aforementioned cross-linking by the remaining dienyl groups exceeds the decross-linking by the thermal degradation of the peroxy bond at 80 °C and at 110 °C for a short time. Furthermore, the side reactions of the peroxy radicals such as hydrogen-abstraction followed by coupling result in the formation of new cross-linking points (21). Contrary to the case of PP-MS, heating at 110 °C for 2 h is required to effectively reduce the lap-shear strength for a glass joint bonded by the PP-network PEG-D. The PP-network PEG-D contains a peroxy bond only at the cross-linking points and the physical properties of the adhesive layer are less sensitive to the degradation than for the main-chain degradable PP-MS. Furthermore, the PP-network PEG-D releases the linear PEG chains as the degradation product, which does not act as a plasticizer.

Main-Chain Degradable Network Polyperoxides. The network PP-HES was formed by the reaction of the hydroxy functionalized PP-HES and bifunctional isocyanate, TDI, and was investigated as main-chain degradable network polymers (Scheme 3). In our previous study, it was revealed that the main-chain degradable network polyperoxides are more readily degraded than the cross-linking point degradable network polyperoxides (21). Moreover, the urethane group formed by the reaction of PP-HES and TDI results in hydrogen-bonding with another urethane group and/or aluminum substrate, and thus a high lap-shear strength is expected. Figure 8 and Table 4 show the representative lap-shear strength-displacement curves and lap-shear strength

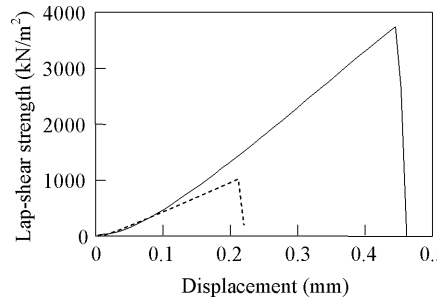


FIGURE 8. Representative lap-shear strength-displacement curves of aluminum joints bonded by network PP-HES; [−OH]:[-NCO] = 100:100 before (—) and after (---) heating at 110 °C for 2 h.

Table 4. Results of Lap-Shear Strength Test of Aluminum Specimen Bonded by Network PP-HES

	lap-shear strength (kN/m^2)		
[−OH]:[−NCO]	before heating	after heating[a]	relative lap-shear strength[b]
100:100	4180 ± 1380	890 ± 250	0.21
100:50	4310 ± 1540	1260 ± 180	0.29
100:25	2030 ± 520	>3080[c]	>1.52
100:10	580 ± 170	n.d.[d]	
100:100[e]	3690 ± 580	1140 ± 150	0.31

[a] At 110 °C for 2 h. [b] The value obtained after heating at 110 °C for 2 h relative to that before heating. [c] The measurement was carried out using a 1 kN (at maximum) load cell with one test joint. [d] Not determined due to too weak an adhesion strength. [e] Glycerol was added; [−OH in PP-HES]:[−OH in glycerol] = 73:27.

of aluminum joints bonded by the network PP-HES, in which the stoichiometric TDI, i.e., [−OH]:[−NCO] = 100:100, was used (34). The obtained lap-shear strength (= 4180 ± 1380 kN/m^2) was as high as that of the hot-melt adhesive (= 3500−7000 kN/m^2) (25). The failure mode was the combination of adhesive and cohesive failures (see the Supporting Information). The network PP-HES was not swollen in chloroform. This suggests that the degree of cross-linking was very high. After heating at 110 °C for 2 h, the value of the lap-shear strength decreased and the adhesive failure became the major failure mode (see the Supporting Information). Concurrently, a marked decrease in the effective adhered area was observed. The tandem action of the thermal degradation of the polyperoxide and the decreased adhered area effectively decreased the lap-shear strength. It was expected that the decrease in the adhered area is due to the reduced interaction between the adhesive layer and aluminum during heating. It was reported that the unreacted isocyanate group does not participate in the cross-linking during the thermal degradation (21), and thus volume shrinkage due to further cross-linking by the remaining hydroxy and isocyanate group can be ruled out.

In our previous study, it was shown that the higher degree of cross-linking resulted in an adverse degradation by heating due to side reactions such as cross-linking (21). To decrease the degree of cross-linking, a lower stoichiometric amount of TDI was used (Table 4). The result of the lap-shear strength test obtained at [−OH]:[−NCO] = 100:50 was very similar to that obtained at [−OH]:[−NCO] = 100:100 (see the Supporting Information). In contrast, at [−OH]:[−NCO]

Table 5. Effect of Heating Conditions on the Results of the Lap-Shear Strength Test of Aluminum Specimen Bonded by Network PP-HES

temperature (°C)	time (h)	lap-shear strength (kN/m^2)	relative lap-shear strength[a]
[b]	[b]	4180 ± 1380	1.00
80	0.5	3750 ± 1510	0.90
80	1	3420 ± 280	0.82
80	2	3200 ± 1380	0.77
110	0.5	2060 ± 710	0.49
110	1	1020 ± 250	0.24
110	2	890 ± 250	0.21

[a] The value obtained after heating relative to that before heating. [b] Specimen before heating.

= 100:25, the network PP-HES behaved as PSAs before heating due to the low degree of cross-linking (see the Supporting Information). After heating, the lap-shear strength had increased. Interestingly, no significant decrease in the adhered area was observed after heating (see the Supporting Information). The lower TDI content resulted in a low degree of cross-linking and more remaining hydroxy groups which interact with the surface of the aluminum plate which prevents the aggregation of the adhesive layer during heating. It is deduced that under the conditions of [−OH]:[−NCO] = 100:25, the lap-shear strength is not simply decreased by the thermal degradation. In the presence of a small amount of TDI, i.e., [−OH]:[−NCO] = 100:10, the network PP-HES also behaved as PSAs and the adhesive strength was effectively decreased after heating. Again, no significant decrease in the adhered area was observed after heating. In this case, the adhesive strength was effectively decreased by the favorable degradation of the polyperoxide without any decrease in the adhered area. The values of the lap-shear strength (= 580 ± 170 kN/m^2) before heating was much higher than that of the linear PP-MS due to the moderately cross-linked structure. This value is lower than acrylic foam tape (= 1400 kN/m^2) and higher than office tape (35−70 kN/m^2) (25). As another approach to reduce the degree of cross-linking, a reactive diluent, glycerol, was added. A result similar to the cases of [−OH]:[−NCO] = 100:100 and 100:50 was obtained. It seems that above a certain degree of cross-linking threshold, the network PP-HESs show a strong adhesive strength, which is effectively reduced by heating, whereas below the threshold level, the network PP-HESs act as PSAs, in which the adhesion properties after heating depend on the amount of the cross-linker.

The dependence of the lap-shear strength of aluminum joints bonded by the network PP-HES obtained in the presence of a stoichiometric amount of TDI, i.e., [−OH]:[−NCO] = 100:100, on the heating conditions was investigated (Table 5). Contrary to the case of PP-network PEG-D, with an increasing heating time at 80 °C, a gradual decrease in lap-shear strength value was observed. More pronounced decreases were observed at 110 °C, and a 1 h heating was sufficient to effectively decrease the lap-shear strength. As expected, the main-chain degradable network PP-HES is more readily degraded than the cross-linking point degradable PP-network PEG-D by heating.

CONCLUSIONS

Three types of readily degradable polyperoxides, linear and network polyperoxides, were applied to dismantlable adhesion and their adhesive behavior was investigated in detail. The linear polyperoxide, PP-MS, behaved as a PSA because of its low T_g. The shear holding power and 180° peel strength immediately decreased upon heating at 70 °C, which is much lower than the initial degradation temperature of PP-MS. It was revealed that the low-molecular-weight products from PP-MS behaved as a plasticizer and the degradation of a small portion of PP-MS resulted in a significant decrease in the cohesive force. UV irradiation also decreased the shear holding power of PP-MS. The PP-network PEG-D, which has peroxy bonds at the cross-linking points, showed a higher adhesive strength than PP-MS due to its three-dimensional network structure. To effectively decrease the adhesive strength of the PP-network PEG-D, heating at 110 °C for 2 h was required. The network PP-HES, which has peroxy repeating units in the main-chain, showed a much higher lap-shear strength than that of the PP-network PEG-D by a factor of more than ten. The lap-shear strength of the network PP-HES more readily decreased than the case of the PP-network PEG-D. The adhesive behavior of the network PP-HES depended on the addition amount of the cross-linker. The polyperoxides investigated in this study showed potential for use in dismantlable adhesion.

Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Oyane, A.; Ishizone, T.; Uchida, M.; Furukawa, K.; Ushida, T. *Adv. Mater.* **2005**, *17*, 2329–2332.
(2) Tajima, S.; Komvopoulos, K. *J. Appl. Phys.* **2007**, *101*, 014307/1−014307/8.
(3) Song, J.; Tranchida, D.; Vancso, J. *Macromolecules* **2008**, *41*, 6757–6762.
(4) Befahy, S.; Lipnik, P.; Pardoen, T.; Nascimento, C.; Patris, B.; Bertrand, P.; Yunus, S. *Langmuir* **2010**, *26*, 3372–3375.
(5) Muller, C.; Luders, A.; Hoth-Hannig, W.; Hannig, M.; Ziegler, C. *Langmuir* **2010**, *26*, 4136–4141.
(6) Stevens, E. S. *Green Plastics*; Princeton University Press: NJ, 2002.
(7) Dorgan, J. R.; Braun, B.; Wegner, J. R.; Knauss, D. M. In *Degradable Polymers and Materials: Principles and Practice*; Khemani, K. C.; Scholz, C., Eds.; ACS: Washington, DC, 2005.
(8) Schnabel, W. *Polymer Degradation: Principles and Practical Applications*; Macmillan Publishing: New York, 1981, pp 125−126.
(9) Berg, J. C. In *Surface, Chemistry and Applications*; Chaudhury, M.; Pocius, A. V., Eds.; Elsevier: Amsterdam, 2002; pp 1−73.
(10) Aubert, J. H. *J. Adhes.* **2003**, *79*, 609–616.
(11) Wang, R.; Xiao, X.; Xie, T. *Macromol. Rapid Commun.* **2010**, *31*, 295–299.
(12) Wang, R.; Xie, T. *Langmuir* **2010**, *26*, 2999–3002.
(13) Luo, X.; Lauber, K. E.; Mather, P. T. *Polymer* **2010**, *51*, 1169–1175.
(14) Matsumoto, A.; Higashi, H. *Macromolecules* **2000**, *33*, 1651–1655.
(15) Hatakenaka, H.; Takahashi, Y.; Matsumoto, A. *Polym. J.* **2003**, *35*, 640–651.
(16) Taketani, S.; Matsumoto, A. *Chem. Lett.* **2006**, *35*, 104–105.
(17) Matsumoto, A.; Taketani, S. *J. Am. Chem. Soc.* **2006**, *128*, 4566–4567.

(18) Taketani, S.; Matsumoto, A. *Macromol. Chem. Phys.* **2004**, *205*, 2451–2456.
(19) Sugimoto, Y.; Taketani, S.; Kitamura, T.; Uda, D.; Matsumoto, A. *Macromolecules* **2006**, *39*, 9112–9119.
(20) Kitamura, T.; Matsumoto, A. *Macromolecules* **2007**, *40*, 6143–6149.
(21) Mihashi, A.; Tamura, H.; Sato, E.; Matsumoto, A. *Prog. Org. Coat.* **2010**, *67*, 85–91.
(22) Sato, E.; Kitamura, T.; Matsumoto, A. *Macromol. Rapid Commun.* **2008**, *29*, 1950–1953.
(23) Fujioka, T.; Taketani, S.; Nagasaki, T.; Matsumoto, A. *Bioconjugate Chem.* **2009**, *20*, 1879–1887.
(24) Sato, E.; Matsumoto, A. *Chem. Rec.* **2009**, *9*, 247–257.
(25) Everaerts, A. I.; Clemens, L. M. In *Surfaces, Chemistry, and Applications*; Chaudhury, M.; Pocius, A. V., Eds.; Elsevier: Amsterdam, 2002, pp 466—468.
(26) The weight of jig, ca. 200 g, was applied on the test specimen for all the lap-shear measurement and was not considered in this result.
(27) Voyutskii, S. S.a., Ed. *Autohesion and Adhesion of High Polymers*; John Wiley & Sons: New York, 1963.
(28) Matsumoto, A.; Taketani, S. *Chem. Lett.* **2004**, *33*, 732–733.
(29) Gilbert, B. C.; Dobbs, A. J. In *Organic peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1967; Vol. III, pp 278—279.
(30) 300 mm/min (ASTM) are recommended as peel rate.
(31) Aubrey, D. W.; Welding, G. N.; Wong, T. *J. Appl. Polym. Sci.* **1969**, *13*, 2193–2207.
(32) Generally speaking, PSAs have T_g values ranging 30 to 70°C below room temperature.
(33) Kitamura, T.; Matsumoto, A. *Macromolecules* **2007**, *40*, 509–517.
(34) Glass specimen bonded by the network PP-HES resulted in substrate fracture.

AM1004392