

Development of Pressure-Sensitive Adhesives Degradable on Ultrasonic Irradiation

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We have developed novel pressure-sensitive adhesives (PSAs) which could be peeled off easily on ultrasonic irradiation as external stimuli. The PSAs were composed of acid-degradable polyurethanes and microcapsules containing a thermal acid generator (TAG). Three layered (w/o/w) type microcapsules containing a TAG were prepared by coacervation method. Generation of acid from the microcapsules and PSA layers on ultrasonic irradiation in water was confirmed by pH changes. Peel strength of PSAs containing the microcapsules decreased from 10 to 1 N/20mm on ultrasonic irradiation in water at 28 kHz for 20 min. The peel strength of PSAs containing the microcapsules was constant on heating up to 80 °C for 1 h, while that decreased on heating above 80 °C. These results suggest that acid was generated but kept in microcapsules on heating up to 80 °C, and the acid was released from microcapsules when PSAs were ultrasonic irradiated or heated above 80 °C.

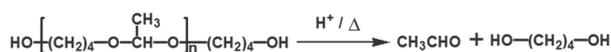
Keywords: Pressure-sensitive adhesive, Ultrasonic irradiation, Microcapsule, Acid-degradable polyurethane, Thermal acid generator

1. Introduction

Pressure-sensitive adhesives (PSAs) are often used in tapes, labels, glues, and a wide variety of other products utilizing their viscoelastic character [1]. Recently, PSAs which can be removed from substrates easily by external stimuli such as UV irradiation [2-4], heat [5-7], and electrical voltage [8,9] were proposed in manufacturing of electronics and automobile.

We have reported PSAs which can be peeled off with light and heat as external stimuli. Photolabile crosslinkers [10,11] containing both polymerizable methacrylates and degradable *O*-acyloxime moieties in a molecule were newly prepared and used in PSAs peelable on UV irradiation [12-14]. Thermally peelable PSAs composed of thermal acid generators (TAGs) and acid-degradable polyurethanes were also proposed [15]. The polyurethanes were obtained from diols which were degradable into acetaldehyde and 1,4-butanediol as shown in Scheme 1 [16]. The PSAs could be peeled

off from substrates easily on heating at different temperatures, reflecting the thermal decomposition temperature of used TAGs [15].



Scheme 1. Degradation reaction of diol.

Recently, ultrasonic irradiation has been applied as a trigger to induce preparation, modification, and degradation of polymers as observed in recent reviews [17-21]. The degradation of polyethylenes [22,23], polyamides [24], polyacrylates [25,26], and epoxy-amine thermosets [27] were reported. However, there are few reports regarding PSAs that were peeled off by using ultrasonic irradiation.

In this study, we propose PSAs composed of a microencapsulated TAG and acid-degradable polyurethanes that are peelable by using ultrasonic irradiation. The effects of ultrasonic irradiation and heat treatment on the stability of microcapsules and

the peel strength of PSAs are investigated.

2. Experimental

Microcapsules containing a TAG (SI-80, Sanshin Chemical Industry, Japan) were prepared by coacervation method as shown in Fig. 1 [28]. To yield water in oil (o/w) microcapsules, 100 mL of ion exchanged water containing 2.00 g of sodium alginate (TCI, Japan) and 1.00 g of a TAG were mixed with 100 mL of dichloromethane solution containing 8.00 g of poly(methyl methacrylate) (PMMA, M_n : 84,000, M_w : 126,400, Wako Chemical, Japan), and homogenized for 10 min. To the mixture, 400 mL of water containing 4.00 g of poly(vinyl alcohol) (PVA, KANTO Chemical, Japan) was added and stirred for 30 min. After removal of dichloromethane in reduced pressure, resulting powders were washed with water several times using centrifugal separation. After drying, three layered (w/o/w) type microcapsules were obtained which were characterized by a Hitachi High-Technologies S-4800 field emission scanning electron microscope (FE-SEM) and an Otsuka Electronics ELS-8000HW particle size analyzer.

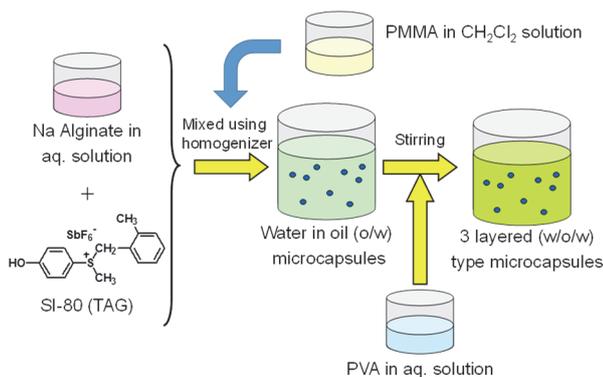
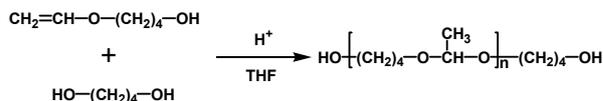


Fig. 1. Preparation of microcapsules containing a TAG by coacervation method.

Degradable diol was prepared as shown in Scheme 2 [16]. In a flask, 50.00 g of 4-vinylxybutan-1-ol (TCI, Japan) and 1.71 g of 1,4-butanediol (Wako Chemical, Japan) were dissolved in 200 mL of THF. To the solution, a small amount of *p*-toluenesulfonic acid (TCI, Japan) was added and stirred at room temperature for 24 h. Repeating decantation of supernatant layer after adding THF several times, the mixture was rotavapped. The residue was washed with saturated sodium bicarbonate aqueous solution to obtain ca. 40 g of colorless tar. ^1H NMR of obtained diol is shown in Fig. 2. The diol was used in the next step without further purification.



Scheme 2. Synthesis of degradable diol.

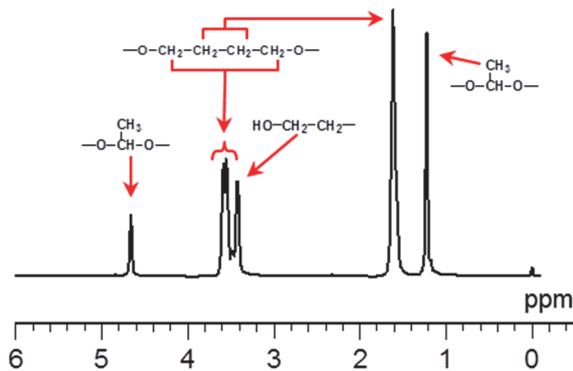


Fig. 2. ^1H NMR (CDCl_3) spectra of degradable diol.

To 7.00 g of 50 wt% acetone solution of polyester polyol (OD-X-2560, M_w : 2000, hydroxyl value: 53-59 mgKOH/g, DIC, Japan), 1.50 g of the diol, 0.92 g of a multifunctional isocyanate (Coronate 2365, isocyanate content: 22.3 %, Tosoh, Japan), and a drop of catalyst (TN-480, Sakai Chemical, Japan) were added and stirred at room temperature for 24 h to obtain a polyurethane solution. The molar ratio of isocyanate and hydroxyl groups of polyester polyol in the solution was set to 1.0 : 0.7, and the weight ratio of polyol and diol was 0.7 : 0.3.

PSA-coated films were obtained by coating the formulation composed of 0.50 g of microcapsules and 10.00 g of the polyurethane solution. The formulation was cast on PET films with an applicator and dried overnight in a dry desiccator at room temperature to yield ca. 50 μm thickness PSA films. The PSA films were cut into 20 mm x 150 mm, covered with PET plate on SUS substrates, and pressed by a 2 kgf rubber roller.

For the evaluation of peel strength, the films were heated in an oven. Then, ultrasonic irradiation was carried out in an Asone VS-10003 ultrasonic washing machine at 28 kHz for 30 min in water. 180° peel strength was evaluated with 100 N loadcell at 300 mm/min by using an Instron 5582 Material Testing System.

In the detection of generated acid, 1.00 g of microcapsules were dispersed in 10 mL of ion exchanged water in a reagent bottle and subjected to ultrasonic irradiation. Then, pH of the solution was measured by using a Horiba F-23 pH/ION meter.

For the acid detection from microcapsules in PSA layers, we used PSA films containing three-fold excess of microcapsules were introduced. After

ultrasonic irradiation for 30 min, the PSA layers were dissolved in acetone, and the solvents were removed in reduced pressure. To the residue, a small amount of water was added, and its pH was measured with universal test paper.

3. Results and discussion

We designed peelable PSAs composed of acid-degradable polyurethanes and microcapsules containing a TAG. Two kinds of diols were used for the acid-degradable polyurethanes: one contains acid-degradable linker unit, and the other is polyester polyol oligomer that contributes to adhesive character. A used TAG (SI-80) has antimonate anion and is known to generate strong acid around 80 °C.

First, we prepared three layered microcapsules containing a TAG in conventional method [28]. SEM image and particle size distribution of the obtained microcapsules are shown in Fig. 3. The average particle diameter was 1.1 μm. After heating at 80 °C for 1 h, similar SEM image of microcapsules was obtained, showing their stability at 80 °C.

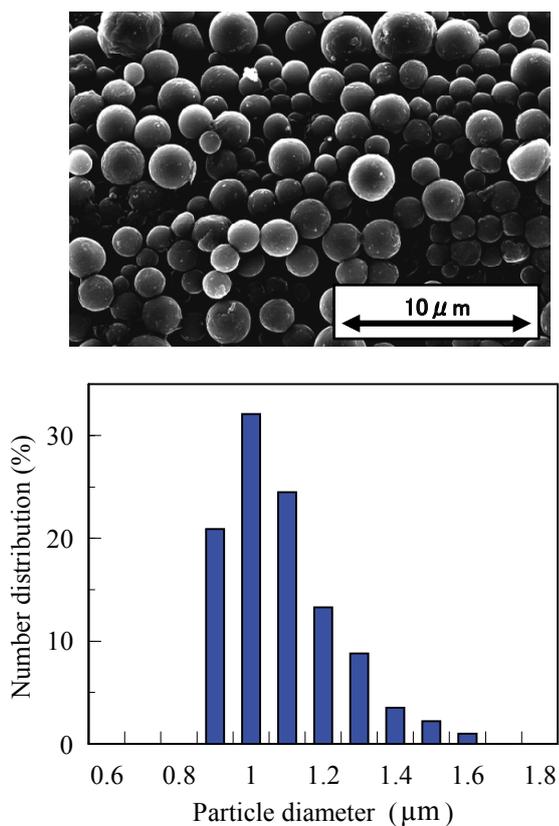


Fig. 3. SEM image and particle size distribution of microcapsules containing a TAG.

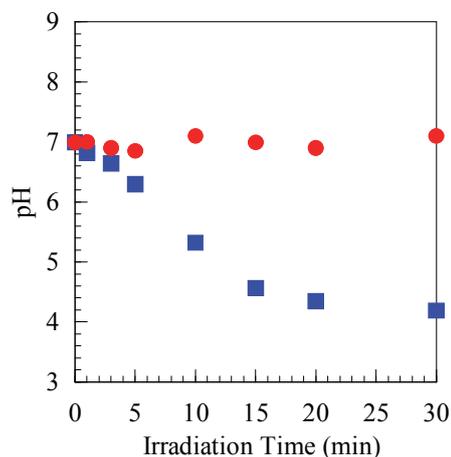


Fig. 4. pH changes of slurry of microcapsules (■) with and (●) without a TAG on ultrasonic irradiation at 28 kHz in water.

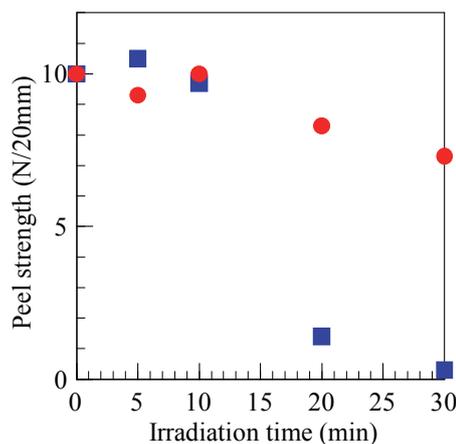


Fig. 5. Changes of peel strength of PSAs containing microcapsules (■) with and (●) without a TAG on ultrasonic irradiation at 28 kHz in water.

In the next step, the degradable property of the microcapsules on ultrasonic irradiation in water was investigated. As shown in Fig. 4, slurry of microcapsules without a TAG afforded constant pH values on ultrasonic irradiation, although the values for microcapsules containing a TAG decreased. When the slurry was heated at 80 °C for 30 min, pH was 7. Previously, we have confirmed that PSAs composed of the same polyurethanes and 1 wt% of SI-80 showed the decrease in peel strength to ca. 0 N/20mm on heating at 80 °C for 10 min, showing SI-80 generated acid on heating at this temperature in PSA layers [15]. These results indicate that acid was generated in the microcapsules on heating at 80 °C, and ultrasonic irradiation was necessary to release the acid.

Table 1. Peel strength of PSAs.

Heating ^a temperature (°C)	Peel strength (N/20mm)			
	Without microcapsules		With microcapsules containing a TAG	
	Before ultrasonic irradiation ^b	After ultrasonic irradiation ^b	Before ultrasonic irradiation ^b	After ultrasonic irradiation ^b
No heat	14.0	14.0	14.3	0.8
60	14.0	14.2	14.3	1.0
80	13.9	13.0	14.5	0.9
100	9.5	9.5	0.9	0.6
120	6.4	6.2	1.1	0.7
150	1.7	1.5	0.9	0.8

a) For 1 h.

b) 28 kHz for 30 min.

Figure 5 shows peel strength changes of PSAs on ultrasonic irradiation in water. In the absence of a TAG, the remarkable reduction was not observed. However, when we used the PSAs with microcapsules containing a TAG, the peel strength decreased on ultrasonic irradiation for 20 and 30 mins, and their failure mode was cohesive. Also, pH of the water dissolving PSAs after the ultrasonic irradiation was about 4, which indicates the generation of acid in PSA layers. These results suggest that acid was released from the microcapsules, caused main chain scission of the polyurethane, which led to a decrease in cohesive force of PSA layers.

The effects of heating and ultrasonic irradiation on peel strength of PSAs are summarized in Table 1. In the absence of microcapsules, peel strength was constant till 80 °C and gradually decreased at higher temperature in spite that ultrasonic irradiation was carried out or not. This result shows the polyurethane was stable on heating below 80 °C and ultrasonic irradiation.

In the presence of microcapsules, peel strength was almost 1 N/20mm except on heating at 80 °C and below before ultrasonic irradiation. These results suggest that generation of acid was possible when PSA films were heated higher than 80 °C and ultrasonic irradiated. The acid was generated in microcapsules but not released on heating at 80 °C alone.

From these data, we can summarize as shown in Fig. 6. There were two paths of free acid generation: (i) on ultrasonic irradiation and heating higher than 80 °C, acid generated and was released from microcapsules, and (ii) on heating at 80 °C, acid generated but was kept in microcapsules. Then,

ultrasonic irradiation led to degrade the microcapsules, and the acid was released. The free acid induced to degrade the polyurethane.

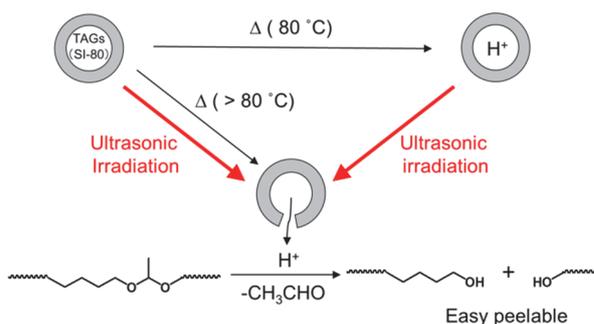


Fig. 6. Generation of free acid in PSAs.

4. Conclusion

The degradation of PSAs composed of acid-degradable polyurethanes and microcapsules containing a TAG on ultrasonic irradiation were demonstrated. A TAG was introduced in microcapsules, and acid was not released from microcapsules on heating at 80 °C in spite that acid generated. However, on heating higher than 80 °C and ultrasonic irradiation, the peel strength decreased due to resulting acid from microcapsules.

These results indicate that the easy peelable PSAs on ultrasonic irradiation are useful as newly functional materials.

Acknowledgement

This work was supported by Iketani Science and Technology Foundation, and JSPS KAKENHI Grant Number 26340082.

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