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Contact time dependence of tack for crosslinked polyacrylic pressure-sensitive adhesives with two different molecular structures

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ABSTRACT

The influence of molecular structure of pressure-sensitive adhesive on the wetting to adherend surface was investigated. For this purpose, crosslinked poly(*n*-butyl acrylate-acrylic acid) (A) and poly(2-ethylhexyl acrylate-acrylic acid) random copolymer (B) with an acrylic acid content of 5 wt% and various crosslinking degrees were used. Tack was measured by a probe tack test with a debonding rate of 10 mm/s and various contact times ranging from 3 to 30,000 s. The probe was made of stainless steel (SS). The tack increased with contact time and the degree of tack rising was B > A. The tack was A > B below the contact time of about 100 s, whereas it was B > A above 100 s. The order of molecular mobility was B > A from pulse nuclear magnetic resonance analysis, so the wettability to adherend surface became B > A. This is the reason why tack was B > A above 100 s. The interfacial tension at a water/toluene interface was decreased more effectively by A than B. This result indicates that the acrylic acid unit in A forms the interaction with the high energy surface such as SS in short contact time. The 2-ethylhexyl group is bulker than the *n*-butyl group. The bulky group promotes steric hindrance for the interaction of the acrylic acid unit. This seems to be the reason why tack was A > B below 100 s.

1. Introduction

The important feature of a pressure-sensitive adhesive (PSA) tape is adhering immediately under light pressure and short contact time. This property is named “tack”. The American Society for Testing and Materials (ASTM) defines tack as “the force required to separate an adherend and an adhesive at the interface shortly after they have been brought rapidly into contact under light load of short duration” [1]. To evaluate the tack property of PSA, one probe tack tester is adopted in the ASTM. This tester was proposed by Hammond [2] and is commercially available as the Polyken tack tester [3].

However, a tack test deviates more widely from the above mentioned original definition. Zosel [4], Creton et al. [5–9], and others [10–15] used the probe tack test to clarify the adhesion mechanism for PSA. Zosel [4] suggested that the work of adhesion measured from the area under the force–displacement curve and the shape of the curve are more important than the tack value for understanding the adhesion mechanism. Creton et al. [5] observed deformation of the adhesive layer (cavitation and fibrillation) during the probe tack test using a high-speed camera. When interfacial adhesion was weak, interfacial peeling occurred preferentially and no void formation was observed in the adhesive layer. The stress–displacement curve was sharp. In contrast, when interfacial adhesion was sufficient, many voids formed and the stress–displacement curve showed a sharp peak with a plateau. Thus, they observed peel behavior during probe tack test in detail. The adhesion strength of PSA is affected by two factors: the development of interfacial adhesion and the cohesive strength of PSA [16–19]. The adhesion strength is dependent on the multiplication of these two factors. To clarify the adhesion mechanism of PSA, it is also important to know the relative contribution of these two factors on tack. However, Creton et al. often used high pressure on the PSA and a thick adhesive layer (approximately 200 μm) to obtain sufficient interfacial adhesion [5] and measured tack at an extremely slow rate, such as 1 μm/s [7]. The original purpose of a tack test is to estimate the interfacial adhesion acquired by the short contact time and light pressure as explained above. Under the condition by Creton et al., the interfacial adhesion is sufficient and they investigated the deformation behavior of PSA.

Previously [20], in order to investigate the wetting of PSA to the adherend surface, the contact time dependence of tack was measured with the contact time in the range from 1 to 30,000 s under a light contact condition. The probe tack tester used was based on the

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specification of the above mentioned ASTM standard [1]. The PSA used was a crosslinked poly(n-butyl acrylate-acrylic acid) random copolymer [P(BA-AA)] with an acrylic acid content of 5 wt% with various crosslinking degrees. The adhesive thickness was approximately 50 μm. Tack was measured using a probe tack tester with a debonding rate of 10 mm/s. The relation between tack and contact time was plotted. The tack increased with contact time. This gradient, namely the increase in tack with contact time is considered to be the wetting rate of PSA to the adherend (probe) surface. The degree of tack increase decreased with an increase in crosslinking degree of PSA.

In this study, the influence of the molecular structure of PSA on tack increase was investigated under the tack condition of light contact. For this purpose, the tack properties of both crosslinked poly(2-ethylhexyl acrylate-acrylic acid) random copolymer [P(2EHA-AA)] with an acrylic acid content of 5 wt% with various crosslinking degrees and crosslinked P(BA-AA) were measured. From the obtained results, the influence of molecular structure of PSA on the relative contribution of interfacial adhesion and cohesive strength on tack properties is discussed. Both polymers are widely utilized as PSA. Tobing and Klein [21] compared the viscoelastic properties of PBA and P2EHA. They clarified that their entanglement molecular weights were 21 and 37 kg/mol, respectively. The storage modulus above the glass transition temperature, namely the rubbery plateau region was higher for PBA than P2EHA. This difference should influence the wetting behavior. The adhesive thickness of these two systems in this study was both approximately 30 μm and that for the previously reported crosslinked P(BA-AA) was approximately 50 μm [20]. The influence of adhesive thickness is also discussed from these results.

2. Experimental

2.1. Materials

P(BA-AA) with an AA content of 5 wt% [weight average molecular weight (M_w) of 500,000, polydispersity of 4.9, 40 wt% ethyl acetate solution, Toagosei Co., Ltd., Tokyo, Japan] and P(2EHA-AA) with an AA content of 5 wt% (M_w of 490,000, polydispersity of 4.1, 50 wt% ethyl acetate solution, Fujikura Kasei Co., Ltd., Tokyo, Japan) were used as base polymers. *N*, *N*, *N'*, *N'*-tetraglycidyl-*m*-xylenediamine (Tetrad-X, Mitsubishi Gas Chemical Company, Inc., Tokyo, Japan) was used as a crosslinker. Reagent grade ethyl acetate was used.

2.2. Sample preparation

Predetermined quantities of polymer solution and the crosslinker were mixed, with ethyl acetate added to bring it to the desired concentration. The mixture was sufficiently stirred and the crosslinker was added in concentrations ranging from 0 to 0.024 chemical equivalents (Eq.). Ethyl acetate solutions of PSA were prepared at a solute content of 40 wt%. The solutions were coated on poly(ethylene terephthalate) (PET) sheets (thickness: 38 μm) using an applicator. The cast films were heated at 115 °C for 2 min to evaporate the ethyl acetate, then the film was heated at 30 °C for 10 days to accelerate the crosslinking reaction. The thickness of the resulting PSA layer was measured using a thickness indicator (dial thickness gauge H-MT, Ozaki, Tokyo, Japan) and was determined to be about 30 μm.

2.3. Gel fraction

The PET sheet with coated PSA film on the surface was cut into squares (50 × 50 mm^2) and the weight (w_1) was measured precisely. The PET with PSA film was wrapped in PET mesh (#200) and the surrounding area was sealed with a stapler. This weight was again measured (w_2). The prepared specimens were immersed in toluene at 23 °C for 10 days. The swollen films were then dried at 100 °C for 3 h and the weight was measured (w_3). The remaining PSA on the PET sheet was washed completely with toluene and the weight of only the PET sheet was measured (w_P). The gel fraction was calculated in accordance with Eq. (1).

$$\text{Gel fraction} = \frac{(w_1 - w_p) - (w_2 - w_s)}{w_1 - w_p} \times 100 \tag{1}$$

2.4. Tack

Tack was measured using a probe tack tester (TE-6002, Tester Sangyo Co., Ltd., Saitama, Japan) at 23 °C. This apparatus is based on the above mentioned Polyken tack tester specified by ASTM [1]. A schematic of the test procedure and the measurement component of the probe tack tester are shown in Fig. 1. The probe was cylindrical (5 mm in diameter) and made of stainless steel (SS). PSA tapes were attached to a weight, which was set on a supporting board (a). When the tack measurement was started, the supporting board descended with a displacement rate of 10 mm/s. When the probe pushed the attached PSA tape, contact between the probe and sample adhesive tape begins (b). After a predetermined contact time, the supporting board begins to elevate. Debonding takes place at this time (c). The force–displacement curve during the debonding process was recorded. The contact time was in the range from 1 to 30,000 s. The tack value was calculated from the maximum force value in the curve and the work of adhesion was calculated from the area under the curve. The compression force of the weight was 0.10 N. The displacement rate of the supporting board was 10 mm/s. Hereafter, the displacement rate of the supporting board is denoted as the debonding rate. One sample was measured 8 times. The difference between average value and maximum or minimum value is shown as the error bar. This probe tack test is described in ASTM [1] as a standard test method for PSA tape which is suitable for evaluating the influence of contact time on tack properties under light contact. However, the deformation of a PSA tape takes place when the probe pushed the PSA tape attached to a weight. So, the influence of the deformation of backing material is also included in both tack and work of adhesion. For this reason, the tack and the work of adhesion measured in this report are in what should be called as "an apparent tack" and "an apparent work of adhesion", respectively. So, these values are used only for a relative comparison in this report.

Probes made of poly(tetrafluoroethylene) (PTFE), polypropylene (PP), polyethylene (PE), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), polycarbonate (PC), polyoxymethylene (POM) and glass were used to investigate the influence of adherend type (probe).

2.5. Pulse NMR

In order to evaluate the molecular mobility of PSA, pulse NMR measurements (JNM-MU25, resonance frequency of 25 MHz, JEOL Ltd., Tokyo, Japan) were carried out using the solid echo method at 20 °C as previously reported [22]. In these experiments, the sampling time was 2 ms, the integration was carried out 128 times, the pulse width of the radiofrequency wave was 2.2 μs, the pulse interval was 8.0 μs and the repeat time of the pulse wave was 4.0 s.

The obtained free induction decay (FID) curves were analyzed as follows in accordance with the method proposed by Urahama [23]: the FID amplitude (the signal intensity at 0 ms) was normalized—*i.e.*, the FID curves were corrected to make the FID amplitude constant—and then the normalized FID curves were differentiated. The obtained curve is shown as the relaxation spectrum function $H(\tau)$. The time axis of the analyzed result is shown logarithmically. Thus, when the data measured with a fixed time interval are shown logarithmically, the data points become sparse in the shorter relaxation time region.