

## Probe tack of tackified acrylic emulsion PSAs

Birm-June Kim, Sung-Eun Kim, Hyun-Sung Do, Sumin Kim, Hyun-Joong Kim\*

Laboratory of Adhesion and Bio-Composites, Major in Environmental Materials Science, Seoul National University, Seoul 151-921, Republic of Korea

Accepted 13 February 2006  
Available online 18 April 2006

### Abstract

Water-based acrylic, pressure sensitive adhesives (PSAs) were prepared by addition of aqueous rosin esters dispersions. PSA films were laminated to corona-treated PET film of 50  $\mu\text{m}$  average thickness by transfer-coating. The glass transition temperature ( $T_g$ ) was measured using differential scanning calorimetry (DSC). The probe tack test was conducted using texture analyzer. The tack performance of tackified emulsion PSAs were affected by the  $T_g$  of bulk PSAs, as well as by the miscibility and tackifier contents.

© 2006 Elsevier Ltd. All rights reserved.

*Keywords:* B. Tackified acrylic PSA; B. Water-based acrylic PSA; C. Master curve; D. Miscibility; D. Probe tack;  $T_g$

### 1. Introduction

Water-based acrylic, pressure sensitive adhesives (PSAs) are adhesives that contain aqueous tackifier dispersion and acrylic emulsion as their principal raw materials. They are milky white, odorless liquids with solid contents of 40–60%. In quantitative terms, water-based acrylic PSAs are one of the most important groups of adhesives. They form a film by drying their blends and are usually put to use in PSA labels [1].

The production of acrylic emulsion PSAs continues to increase due to their environmental protection ability, high solids contents and good aging resistance properties [2]. As the use of water-based acrylic emulsion PSAs has increased, various preparation methods for acrylic emulsion PSAs have been presented. Initially, simply emulsion polymerized acrylic PSAs were introduced, then water-based label PSAs for various applications and then highly functional PSAs were patented. In addition, tackifier dispersions for water-based acrylic emulsion PSAs and their formulations with PSAs were investigated [3–7]. A tackifier is a thermoplastic, low molecular weight and high glass transition temperature ( $T_g$ ) polymer modifier. The

addition of a tackifier makes the PSA products wet the substrate to form adhesive bonds [16].

Tack is one of the most important performance for PSAs and is affected by  $T_g$  of the materials, the miscibility of the tackifier and rate of separation [9–14].

This study investigated the miscibility and  $T_g$  of water-based acrylic PSAs tackified with various rosin ester dispersions the softening point of tackifier, esterified type of rosin and tackifier content were investigated by using differential scanning calorimetry (DSC) and optical microscopy. Furthermore, probe tack test was conducted by using a texture analyzer.

### 2. Experimental

#### 2.1. Materials

The water-based acrylic emulsion PSA used was PR-60 (Hanwha Chemical Co. Ltd., S. Korea). The polymer characterization data are given in Table 1. The tackifiers used in this study were Superesters E-650, E-720 and E-730-55 (rosin ester dispersion, Arakawa Chemical Co. Ltd., Japan). The properties of the tackifiers are shown in Table 1. The wetting agent was Aerosol OT-75 (Cytec Co.).

\*Corresponding author. Tel.: +822 880 4784; fax: +822 873 2318.  
E-mail address: hjokim@snu.ac.kr (H.-J. Kim).

Table 1  
 $T_g$  and molecular weight of of water-based acrylic PSA (PR-60) and rosin ester dispersion

Product name	PR-60	E-720	E-730-55	E-650
$M_n^a$	8150	710	1220	900
$M_w^a$	55,300	800	2780	2230
MWD <sup>a</sup>	6.8	1.1	2.3	2.5
$T_g$ (°C) <sup>b</sup>	−49.3	55.4	78.3	103.1
Softening point (°C) <sup>b</sup>	58.0	100	125	160
Solid content (wt%)	—	50.4	55.0	51.0
Main components	—	Glycerol ester of stabilized rosin	Pentaerythritol ester of stabilized rosin	Pentaerythritol ester of polymerized rosin

<sup>a</sup>Measured by GPC.

<sup>b</sup>Measured by DSC.

## 2.2. Preparation of PSAs

Acrylic emulsion/tackifier dispersions were blended in the following blend ratios: 90/10, 80/20, 70/30 and 60/40 wt%. Wetting agent (0.9 wt%) was added in the direct driven stirrer (Tops Misung Co.) with an impeller at 500 rpm and the blends were preserved for 24 h at room temperature. The PSA specimens were prepared by transfer coating, using an automatic film applicator (Kee-Pae Trading Co., S. Korea) at room temperature. A bar coater No. 22 (wetting thickness 50.3  $\mu\text{m}$ ) was used. The PSA label was obtained by application to the siliconized release liner, drying at 100 °C for 5 min, and then laminating to the corona-treated polyethylene terephthalate (PET) film of 50  $\mu\text{m}$  average thickness.

## 2.3. Molecular weight

The weight average molecular weight ( $M_w$ ), number average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of the PSAs were determined by gel permeation chromatography (GPC, Waters Co.).

## 2.4. Thermal properties

$T_g$  was measured using DSC (TA Q-1000). Ten samples were cooled to −85 °C, heated to 150 °C at a heating rate of 10 °C/min in the first scan, immediately quench-cooled to −85 °C and then kept at this temperature. The samples were heated to 150 °C at a heating rate of 10 °C/min in the second scan.  $T_g$  defined in this study was obtained from the second scan to assure reproducible thermograms free from thermal history effects.

## 2.5. Microscopic observation

Some blends were observed under an optical microscope (Zeiss Co. Ltd.) equipped with a camera. The blends were

heated at 100 °C during 10 min followed by cooling to room temperature.

## 2.6. Probe tack

Tack test was conducted using a texture analyzer (Micro Stable Systems, TA-XT2i) with a polished stainless-steel cylinder probe with a diameter of 5 mm. The measurements were carried out at separation rates of 0.01, 0.05, 0.1, 0.2, 0.3, 0.5 and 1 cm/s under a constant pressure of 100 gf/cm<sup>2</sup> and a dwell time of 1 s at room temperature.

## 3. Results and discussion

### 3.1. Thermal analysis

$T_g$  of polymers is exhibited by amorphous regions of partially crystalline polymers when a viscous or rubbery state is transformed into a hard, brittle, glass-like state.  $T_g$  by DSC has been generally used in the determination of blend miscibility. The phase structure of respective blends is assessed by the number of  $T_g$ 's observed in the thermograms. Two transitions are a clear indication of phase separation, while a single  $T_g$  which is located at a temperature intermediate between those of the pure components indicates the miscibility [8].

Figs. 1a and b show the  $T_g$  values of acrylic emulsion PSA (PR-60), wetting agent (OT-75) and three types of

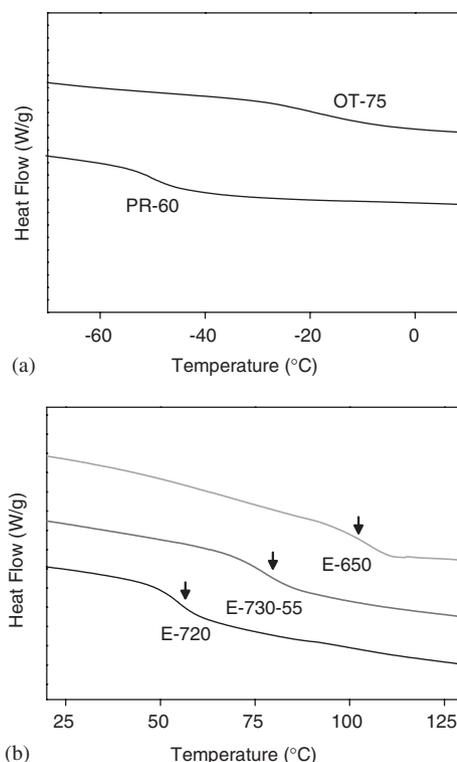


Fig. 1. DSC thermograms of the raw materials for water-based acrylic PSA. (a) Acrylic emulsion PSA and wetting agent. (b) Rosin ester tackifier dispersions.

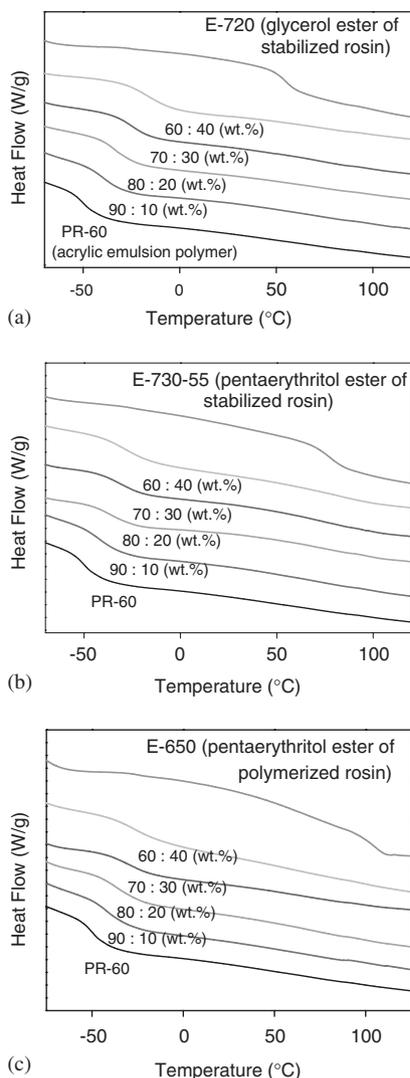


Fig. 2. DSC thermograms of acrylic emulsion PSA/tackifier blends. (a) Acrylic emulsion PSA/E-720 blend. (b) Acrylic emulsion PSA/E-730-55 blend. (c) Acrylic emulsion PSA/E-650 blend.

rosin ester tackifier dispersions (Superesters E-650, E-720 and E-730-55).  $T_g$  of acrylic emulsion PSAs is about  $-50^\circ\text{C}$ .  $T_g$ 's of tackifiers are 55.4, 78.3 and  $103.1^\circ\text{C}$ . This property of the tackifiers might be a result of the esterified types and modifications of rosin. Fig. 2a is composed of heat flow of acrylic emulsions PSA blended with Superester E-720 of different blend ratios.  $T_g$  of these PSAs show gradual changes between  $-48$  and  $-15^\circ\text{C}$ . The behavior of the other tackifiers are similar upto around of 40 wt% tackifier content (Figs. 2b and c). However, the situation is quite different above 40 wt%.

Fig. 3 shows the changes of  $T_g$  curves of acrylic emulsion PSAs tackified with three types of rosin ester dispersion. In Fig. 3a the glycerol-stabilized rosin ester is miscible with acrylic emulsion PSA over the full range of blend ratios, but the others do not show this miscibility. They show partial miscibilities with acrylic emulsion PSA. In Fig. 3b,

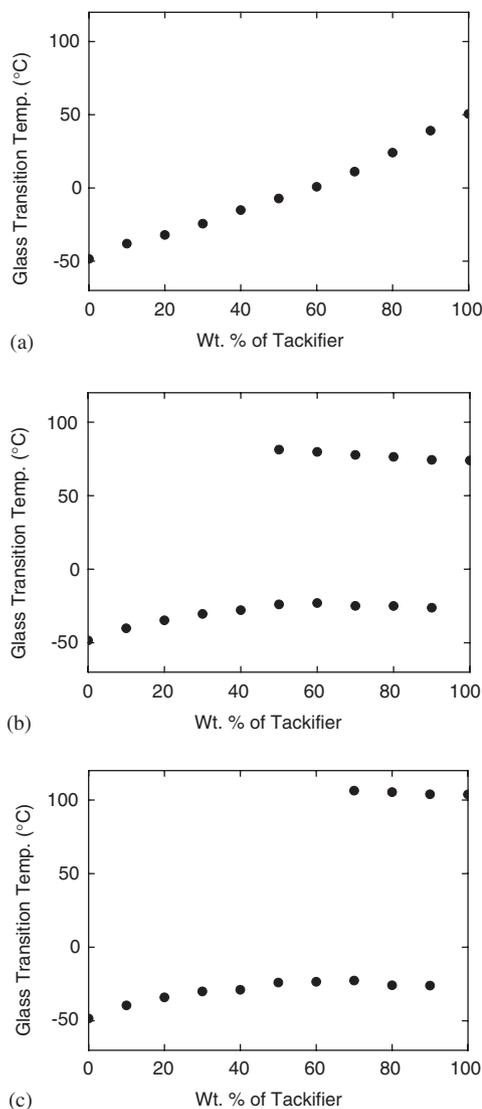


Fig. 3.  $T_g$  versus tackifier content of acrylic emulsion PSA/rosin ester tackifier dispersions with different blend ratios. (a) Acrylic emulsion PSA/E-720 blend. (b) Acrylic emulsion PSA/E-730-55 blend. (c) Acrylic emulsion PSA/E-650 blend.

water-based acrylic emulsion PSA/Superester E-730-55 blend has one  $T_g$  at 40 wt%, but there are two  $T_g$ 's over 40 wt%. In Fig. 3c, water-based acrylic emulsion PSA/Superester E-650 blend has two  $T_g$ 's from 70 to 90 wt%, but there is only one  $T_g$  at lower concentration [18]. Natural rubber/pentaerythritol ester of stabilized rosin blends had shown two  $T_g$ 's in the study of Sherriff et al. [15].

### 3.2. Microscopic observation

The optical micrographs of acrylic emulsion PSA/Superester E-720 are shown in Photo 1a with Superester E-720 content of 40 wt%. This blend system had only one  $T_g$ , which suggests that this blend is a miscible system. The blends of acrylic emulsion PSA/Superester E-730-55 are

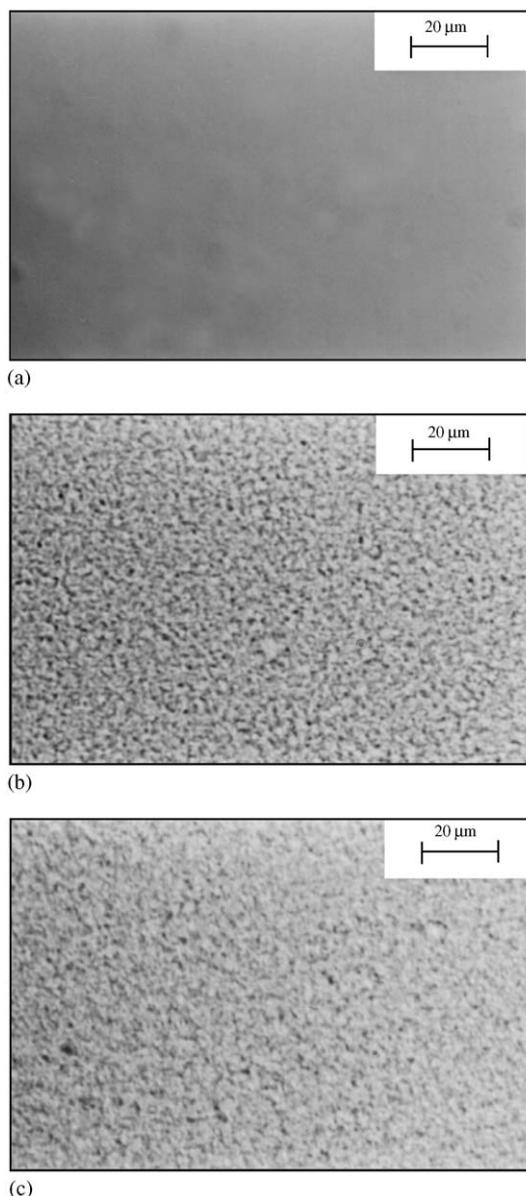


Photo 1. Acrylic emulsion PSA/tackifier dispersion blends (40 wt% tackifier content) ( $\times 1000$ ). (a) Acrylic emulsion PSA/E-720 blend: miscible system. (b) Acrylic emulsion PSA/E-730-55 blend: immiscible system. (c) Acrylic emulsion PSA/E-650 blend: immiscible system.

shown in Photo 1b with tackifier content of 40 wt%. These blends showed the grass-like dispersed tackifier phases by careful observation. The dotted- or grass-like structures in this blend system are thought to be a particle or coagulation of the tackifier, though this blend had one  $T_g$  below 70 wt% tackifier content (by DSC data) and two  $T_g$ 's over 70 wt%. Therefore, this blend system is thought to be immiscible. Photo 1c shows the phase of acrylic emulsion PSA/Superester E-650. This blend system showed the grass-like structures similar to the former immiscible blend (acrylic emulsion PSA/Superester E-730-55). This Superester E-650 blend system also had one  $T_g$  (within 50 wt%

tackifier content) but two  $T_g$ 's (over 50 wt%) by DSC data. Nevertheless, Fujita noted that these blend systems are somewhat immiscible due to the dispersed structure of this 40 wt% tackifier content blend [10].

### 3.3. Probe tack

Probe tack tests are intended to be simulations of thumb or finger tack tests. The tip of a probe is brought into contact with a supported adhesive under low contact pressures for a short time and then pulled away at a fixed rate, during which the peak force of separation is measured [17].

Fig. 4 shows the plots of probe tack versus tackifier content of acrylic emulsion PSAs tackified with three types of rosin ester dispersion blend system. The probe tack of acrylic emulsion PSA/Superester E-720 is increases as the tackifier content increased although the differences of probe tack value between 10 and 20 wt% are small in scale. Acrylic emulsion PSAs/Superester E-720 blends are miscible blends.

In acrylic emulsion PSA/Superester E-730-55 blends the maximum value of probe tack was seen at a tackifier concentration of about 30 wt%, although there was little differences between 20 and 30 wt% tackifier content. The probe tack strength then decreased quickly at 40 wt% content, but was still larger than that at 10 wt% and that of the untackified blend. Also, in acrylic emulsion PSA/Superester E-650 blends the probe tack value peaked at about 20 wt% content, was slightly decreased at 30 wt% content, and was significantly decreased below that of the untackified blend system at 40 wt% content.

On the basis of the DSC data, these two tackifiers (Superesters E-730-55 and E-650) are immiscible with

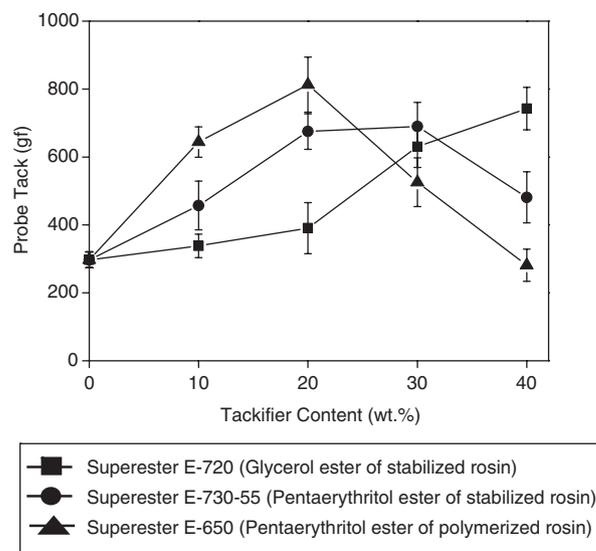


Fig. 4. Probe tack versus tackifier content of three acrylic emulsion PSAs: Superesters E-720, E-730-55 and E-650 (at 10 mm/s).

water-based acrylic emulsion PSA (PR-60). From these probe tack tests, it is thought that the critical decrease of probe tack at high tackifier contents (40 wt%) is due to the immiscibility of the two blend systems. Besides, the high probe tack which was observed at low tackifier content (below 30 wt%) is considered to be a result of the agglomeration of the tackifier dispersed in emulsion.

If the debonding rate is extended to various velocities, the plot of tack strength versus debonding rate exhibits various patterns according to the miscibility of the tackifiers [14]. Fig. 5 shows a steady increase in tack strength as the debonding rate is increased, whereas Figs. 6 and 7 exhibit an increase in low tackifier content. Especially, in Fig. 7 acrylic emulsion PSAs/Superester E-650 blends showed some different features from acrylic emulsion PSAs/Superester E-730-55 blends, even though they all were considered as immiscible blends. The maximum probe tack values of these blend systems shifted toward a lower debonding rate as the tackifier content was increased. We concluded from the results that the tack performances of the tackified emulsion PSAs are affected

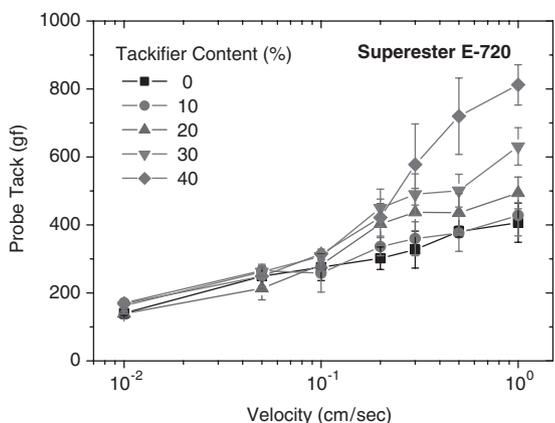


Fig. 5. Master curves of probe tack versus velocity of acrylic emulsion PSA/Superester E-720 blends.

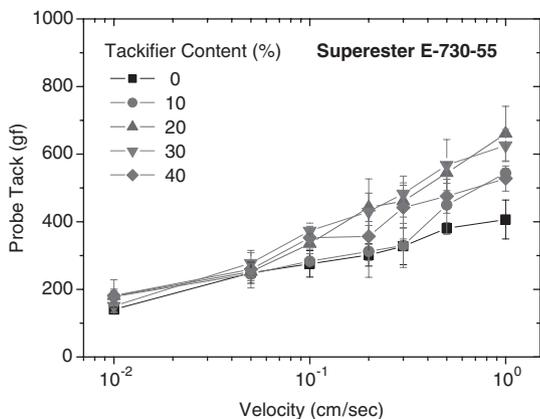


Fig. 6. Master curves of probe tack versus velocity of acrylic emulsion PSA/Superester E-730-55 blends.

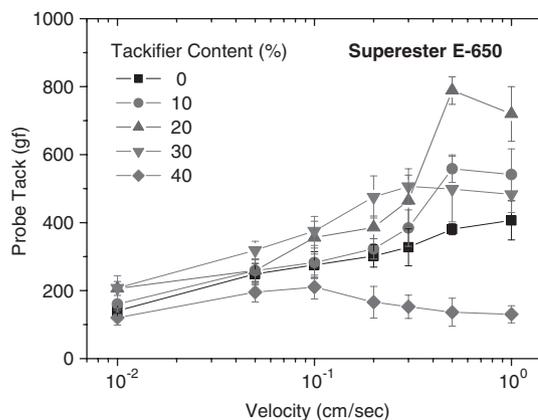


Fig. 7. Master curves of probe tack versus velocity of acrylic emulsion PSA/Superester E-650 blends.

by the amount, miscibility and chemical structure of the tackifier.

#### 4. Conclusions

Water-borne acrylic emulsion PSAs/low  $M_w$  tackifier blends exhibited only one  $T_g$ , whereas water-borne acrylic emulsion PSAs/high  $M_w$  tackifier blends showed two  $T_g$ 's. However, the microscopic structures showed dispersed particles. In miscible blends, the probe tack strength of PSA blends was increased with increasing tackifier content. However, the probe tack strength of immiscible blends differed from that of miscible ones with increasing tackifier content. The maximum probe tack strength of these blend systems was shifted toward a lower debonding rate as the tackifier content was increased. The tack strength of the water-borne acrylic PSAs/tackifier blends was affected by the amount, miscibility and structure of the tackifier.

#### Acknowledgment

This work was supported by the Brain Korea 21 project.

#### References

- [1] Gierenz G, Karmann W. Adhesives and adhesive tapes. Weinheim, Federal Republic of Germany: WILEY-VCH Verlag GmbH; 2001.
- [2] Urban D, Takamura K. Polymer dispersions and their industrial applications. Weinheim: Wiley-VCH Verlag GmbH; 2002.
- [3] Czerepinski RG, Gunderman RE. US patent 762083, 1985.
- [4] Bernard M, Berman St. US patent 686317, 1991.
- [5] Mayer A, Keller P. US patent 819114, 1996.
- [6] Hoff SM, Ternorutsky L. US patent 827857, 1997.
- [7] Hemmings N. Adhes Age 1998;10:40.
- [8] Hatakeyama T, Quinn FX. Thermal analysis fundamentals and applications to polymer science. New York: Wiley; 1999.
- [9] Kim H-J, Mizumachi H. J Appl Polym Sci 1998;69:581.
- [10] Fujita M. PhD. thesis, University of Tokyo, Tokyo, Japan, 1998.

- [11] Fujita M, Kajiyama M, Takemura A, Ono H, Mizumach H, Hayashi S. *J Appl Polym Sci* 1998;70:771.
- [12] Hayashi S, Kim H-J, Kajiyama M, Ono H, Mizumachi H, Zufu Z. *J Appl Polym Sci* 1999;71:651.
- [13] Kim H-J. PhD. thesis, University of Tokyo, Tokyo, Japan, 1995.
- [14] Naruse S, Kim H-J, Tsukatani T, Kajiyama M, Takemura A, Mizumachi H. *J Adhes* 1994;47:165.
- [15] Sherriff M, Knibbs RW, Langley PG. *J Appl Polym Sci* 1973;17:3423.
- [16] Deshpande A, Hyer D, Kemper M, Krajca K, Locko G, Moran M. 25th Annual meeting of the adhesion society, inc. and WCARP- $\alpha$ . 2002.p. 277.
- [17] Satas D. In: Satas D, editor. *Handbook of pressure sensitive adhesive technology*. Warwick: Rhode Island; 1989.