Macromolecular Research, Vol. 14, No. 5, pp 517-523 (2006)

Thermal Conductivity and Adhesion Properties of Thermally Conductive Pressure-Sensitive Adhesives

Jin Kon Kim*, Jong Won Kim, Myung Im Kim, and Min Seok Song

National Creative Research Initiative Center for Block Copolymer Self-Assembly and Department of Chemical Engineering, Pohang University of Science and Technology, Gyungbuk 790-784, Korea

Received May 7, 2006; Revised July 24, 2006

Abstract: The effects of particle content, size and shape on the thermal conductivity (k) and adhesion properties of thermally conductive, pressure-sensitive adhesives (PSAs) were investigated. The matrix resins were thermally crosslinkable, 2-ethylhexyl acrylic polyol and ultraviolet (UV)-curable, random copolymer consisting of acrylic oligomer and various acrylates. We found that k increased with increasing diameter and particle aspect ratio, and was further enhanced due to the reduction of the interfacial thermal barrier when the coupling agent, which increases the adhesion between particles and the matrix resin, was used. On the other hand, adhesion properties such as peel strength and tack of the thermally crosslinkable resin decreased sharply with increasing particle content. However, for UV curable resin, increased particle addition inhibited the decrease in adhesion properties.

Keywords: thermal conductivity, adhesion properties, pressure-sensitive adhesives.

Introduction

Smaller computers and communication devices consume large amounts of power, thereby generating large amounts of heat and significantly reducing the performance and reliability of the devices. This requires the development of methods for effective heat dissipation to the surroundings.[1-5] Although several methods have been available to allow effective heat dissipation, thermally conductive adhesives have been widely used in the industry because of easy thermal path. But, thermally conductive adhesives have other requirements in addition to good thermal conductivity: (1) good insulation for the prevention of electric shorts, (2) good adhesion properties between the substrate and the adhesive, and (3) thermal stability to endure thermal stress resulting from thermal expansion difference between the adhesive and substrate.[6-9]

Thermally conductive adhesive consists of matrix resin and conductive particles. Since the matrix resin has very low thermal conductivity, many conductive particles, such as alumina (Al_2O_3), magnesium oxide, zinc oxide, boron nitride, aluminum nitride, and silicon carbide (SiC), have been widely employed.[6,10] All of these materials exhibit high thermal conductivity and insulator for the electricity. With increasing the amount of particles, the thermal conductivity (k) increases gradually, which is in contrast to the electrical conductivity resin where the electricity suddenly jumps at the percolation threshold concentration of particles.[5,11-17]

Since the above studies[1-5,11-15] investigated k of composites with very high amounts of conductive fillers (at least 50 vol %), these composites could not be used for thermally conductive pressure-sensitive adhesives (TC-PSA) due to poor adhesion between fillers and the matrix polymer. However, the use of TC-PSA is necessary for certain applications for the connection between the heat spreader (or fans) and computer CPU unit,[6] where the adhesion properties of tack or peel strengths become very important in addition to good thermal conductivity. Recently, TC-PSA has been also used for heat resisting seats between aluminum casing and glass panels in the plasma display panels (PDP), since the pan which was previously used to dissipate heat generated inside the equipment cannot be used anymore due to the requirement of thin thickness, lower cost, and negligible noisy. Simple curing type adhesives, not PSA, cannot be used in PDP because the modulus of this adhesive becomes very high after completion of the cure, which cannot maintain the stress resulting from the difference in the heat expansion coefficient between aluminum case and glass panel.[7,8] Although TC-PSA has been used in industry, the relationship between the thermal conductivity and adhesion properties depending on the amount of conducting particles has not been reported in detail in the literature.

In this study, we investigated the effect of particle size and shape, and the coupling agent treatment of particles on k and

*Corresponding Author. E-mail: jkkim@postech.ac.kr

adhesion properties of tack and peel strength of TC-PSA. Two different types of resins were employed: thermal crosslinkable and ultraviolet (UV)-curable matrix resins.

Experimental

Materials and Sample Preparation. Two different thermal conductive particles were employed in this study: 1) alumina (Al_2O_3) with three different particle diameters (5.9 and 86.7 μm purchased from Aldrich Co. and 43.9 μm from Alfa Aesar Co.), 2) and silicon carbide (SiC) with three different shapes (particulate and platelet shapes with a diameter of 38.8 μm, and whisker shape with a diameter of 5.9 μm purchased from Alfa Aesar Co.). Two types of adhesive matrix were used: 1) thermal crosslinkable matrix resin and 2) UV curable matrix resin. Thermal crosslinkable resin consisted of 2-ethylhexyl acrylic polyol (EHAO; M_w=3,600; Soken Co., Japan) which was crosslinked by hexamethylene diisocyanate (HDI) (Desmodur N3400: Bayer Co.) with the aid of a catalyst of dibutyltin dilaurate (Soken Co., Japan). Without any further specification, the molar ratio of crosslinking agent to EHAO resin was maintained to be 1.22. UV curable matrix resin was IRR84 (SK-UCB Co., Korea) consisting of acrylic oligomer, 2-ethylhexyl acrylate (EHA), isobornylacrylate, *N*-vinylpyrrolidone, and trimethylolpropane triacrylate. The photo-initiator for IRR84 resin was 2-hydroxy-2-merhyl-1phenyl-propan-1-one (Darocur 1173: Ciba Co.).

EHAO resin with various contents of particles was mixed inside a vessel having an impeller at a 200 rpm for 2 h at room temperature. Then, HDI was added to this mixture (0.25 g/g resin) and it was mixed again for 45 min under vacuum ~60 torr to remove the bubbles. Finally, 0.1 wt% of dibutyltin dilaurate was added and mixed under vacuum to remove air bubble during the mixing, and then coated onto a releasing paper by using a Doctor Blade to give 1 mm thickness. The EHAO was crosslinked at 60 °C for a week.

To investigate the effect of coupling agent treatment of particles on thermal conductivity, alumina particles were treated by γ-glycidoxy propyl trimethoxy silane (GPS; GELEST Co.). For this purpose, alumina particles were sonicated for 30 min in acetone and rinsed by DI water, and dried under vacuum, immersed into 0.5 wt% of GPS solution in mixture of ethanol/water/acetic acid (PH=4), stirred for 2 h, rinsed by ethanol, and heated at 120 °C under vacuum.

IRR84 resin was mixed with various particles and coated onto PET film by using a Doctor Blade to give 1 mm thickness of the film. Then, the film was irradiated by UV for 30 min under anaerobic condition by using a germicidal UV lamp (G15T8(15W), Sankyo Denki Co.) with a maximum intensity at 253.7 nm.

Thermal Conductivity. The thermal conductivity (k) of conductive particle-filled polymer was measured at 30 °C by using a thermophysical properties analyzer (TPA-501) based on Transient Plane Source/Gustafsson Hot Disk method.[18] A heat pulse is generated for a given time by passage of an electrical current through a very thin metallic foil functioning as a heater and temperature sensor probe unit insulated on both surfaces and embedded between two pieces of the sample. When the temperature rise is measured, the thermal diffusivity (α) of the sample is calculated by the heat conduction model.[18] Then, k is obtained by the expression of $\rho C_p \alpha$,[18] in which the heat capacity (C_p) and the density (ρ) of the particle-filled polymers are measured by differential scanning calorimeter and densitometer, respectively. The sample size for the thermal conductivity measurement was $20 \times 20 \times 0.8$ mm^3 ($L \times W \times T$).

Peel and Tack Properties. The sample (25.4×80 mm^2) for 180°- peel test was prepared by coating of conductive particle-filled adhesives onto a PET backing film with a thickness of 30 μm, and then pressed onto glass substrate twice by a roller with 2 kg. The peel strength was measured according to ASTM D3330 by using a Texture Analyzer (XT2i: Stable Micro System) with the speed of 5 mm/s at room temperature.[19] Six specimens were measured at each amount of thermal conductive PSA. Tack property was measured according to ASTM D2979-01 by using the same Texture Analyzer at the adhesion test mode with crosshead speed of 10 mm/s, contact time of 1 s, and loading force of 9,800 N/m^2. Ten samples were employed for tack measurement.

Morphology. The morphology of particles was investigated by field emission scanning electron microscope (FE-SEM, Hitachi model S-4200), at an operating voltage of 8 kV.

Results and Discussion

Conductivity of Composite. Figure 1 gives the change of the ratio of the thermal conductivity (k_c) of the composite containing alumina to that (k_m) of EHAO resin with amount of alumina for three different diameters (5.9, 43.9, and 86.7 μm). The k_m of EHAO resin after crosslinking was 0.428 W/mK. We could not use higher amounts of alumina than ~0.25 volume fraction due to very low tack and peel properties. It is seen in Figure 1 that k_c/k_m increased with increasing volume fraction of the alumina, but the increase rate was different for different particle diameters. It is known that thermal conductivity of the composite at a given volume fraction of a particle becomes the same regardless of the size of the particle, as long as the degree of the particle dispersion in the matrix is the same. However, there exists an interfacial thermal barrier at the interface between the particles and the matrix resin.[3] Since the surface area of a particle is inversely proportional to the particle size,[1] the interfacial thermal barrier increases with increasing surface area. This concept is also applied to a composite with a par-

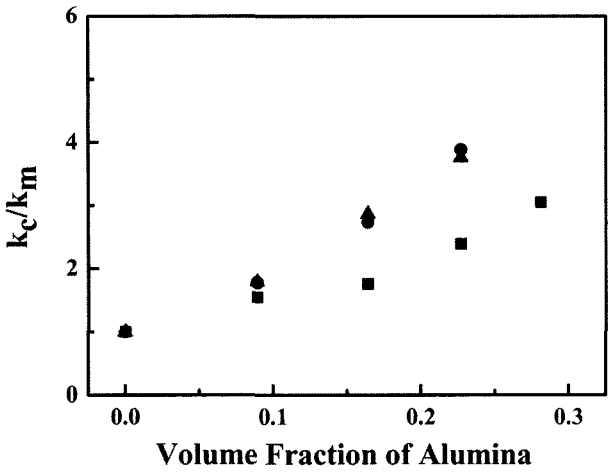

Figure 1. The change of k_c/k_m for EHAO resin with the various amounts of alumina as a function of particle diameter: 5.9 μm (■); 43.9 μm (●); 86.7 μm (▲).

ticle with a broad size distribution when the average particle size is considered. Therefore, k_c with larger particle sizes (43.9 and 86.7 μm) is higher than that of another composite with smaller particle size (5.9 μm).

On the other hand, k_c with particles having a diameter of 43.9 μm is almost the same as that of another composite with particle having a diameter of 86.7 μm. To explain this behavior, the exact shape of three alumina particles was taken by SEM and results are given in Figure 2. Particles having diameters of 5.9 and 43.9 μm have a smooth surface, whereas the particles having a diameter of 86.7 μm have rough one, as clearly shown in Figure 2(d). Because the particles with rough surface increase the overall surface area (and thus the interfacial thermal barriers), k_c of a composite with particles having rough surface becomes smaller. We also consider that the smaller k_c for the composites with rough surface particles might be due to the poor contact area between the resin and particles.

Figure 3 gives the change of k_c/k_m for EHAO resin with the amount of silicone carbide (SiC) having three different shapes (particle, platelet, and whisker whose SEM images are shown in Figure 4). The k_c of a composite with platelet-shaped SiC was higher than that of another with particle-shaped SiC, even though the average size of the two SiCs was the same (38.6 μm). When only an interfacial thermal barrier is concerned, the thermal conductivity of a composite with platelet-shaped SiC should be lower than that of particulate SiC, because the surface area of the former is larger than the latter. However, the experimental result was opposite to this expectation, which leads us to consider

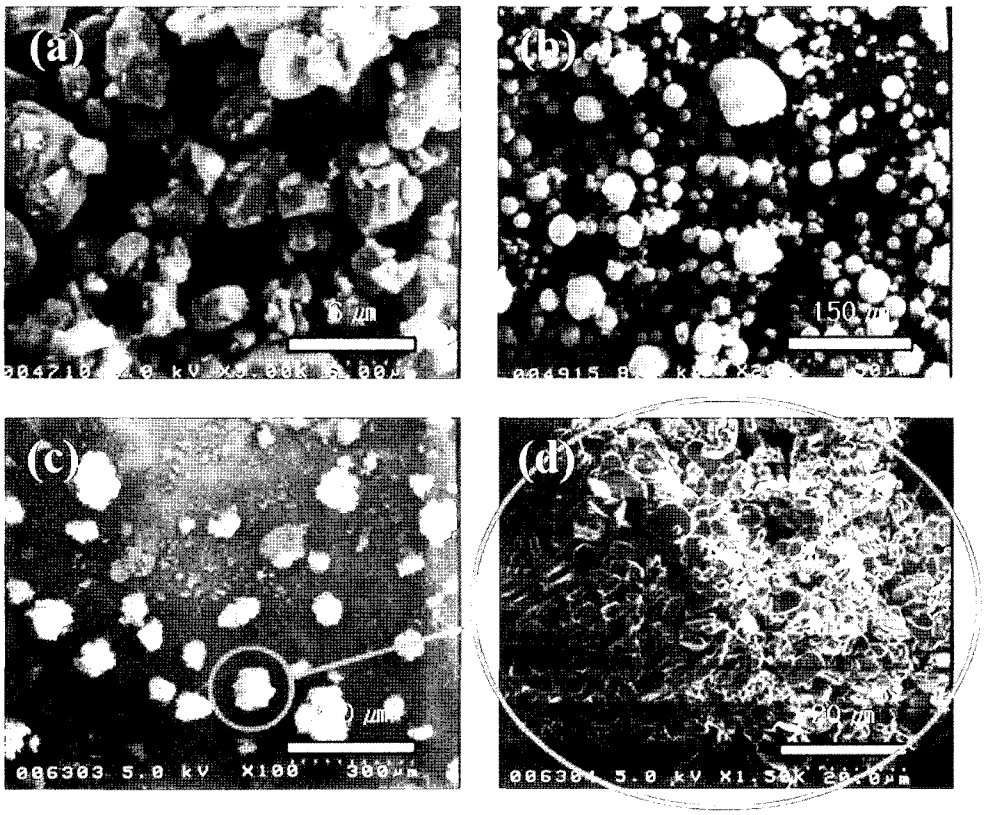

Figure 2. SEM images of alumina used in this study: (a) 5.9 μm, (b) 43.9 μm, (c) 86.7 μm, and (d) is the enlarged SEM image of part (c).

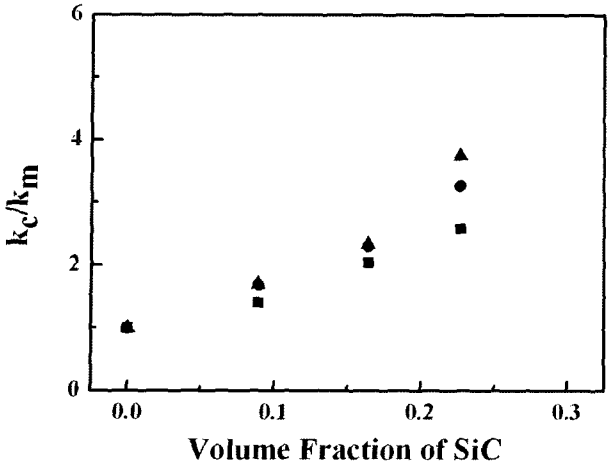

Figure 3. The change of k_c/k_m for EHAO resin with the various amounts of silicon carbide (SiC) as a function of the shape: particulate SiC (■); platelet SiC (●); whisker type SiC (▲).

another effect such as particle shape or the aspect ratio of particles. It is noted that larger electrical conductivity can be obtained for a composite with particles having a higher aspect ratio due to easy current pass for the continuous network at higher aspect ratio. The aspect ratio is defined as the ratio of the longest length (L) and the shortest length (S) of the filler. Since the particles have different sizes, in this study we obtained the aspect ratio by $\left(\sum_{i=1}^{N} L_i^2 / A_i\right)/N$, in which L_i and A_i are the longest length and the surface area of each particle, and N is the total number of particles. From SEM images given in Figure 4, the aspect ratios of the particulate and platelet particles are 2.0 and 3.1, respectively. Thus, the higher conductivity of a composite with platelet-shaped particles compared with particulate particles might be due to the easy connection among particles resulting from the higher aspect ratio. Therefore, the highest k_c at a given amount of SiC particles was due to the largest aspect ratio. This suggests that the aspect ratio of conductive particles becomes more important than particle size for determining k_c.

Figure 5 gives the effect of the coupling agent (GPS) treated alumina particles on k_c/k_m for EHAO resin with various amounts of 86.7 μm alumina. When alumina particles were treated by GPS, k_c increased up to 10% more than that with the same amount of alumina without GPS treatment. Since GPS has an epoxy group at the chain end coupling with oxide layer on the particles, adhesion between particles and matrix increases.[3] Thus, the interfacial thermal barrier reduces, which increases the k_c of a composite.

Adhesion Properties. Good adhesion properties should be required for thermal conductive pressure-sensitive adhesives. Since adhesion properties generally decrease with increasing the amount of conductive particles, the adhesion properties should be balanced with good thermal conductivity. Since the crosslinking agent should be used for EHAO resin, the optimum content of the crosslinking agent was first investigated. Figure 6 gives the changes of probe tack and peel strength with the molar ratio of crosslinking agent to EHAO resin without conductive particles. It is shown that the maximum tack was obtained at a molar ratio of 1.22. On the other hand, the peel strength increased gradually up to a

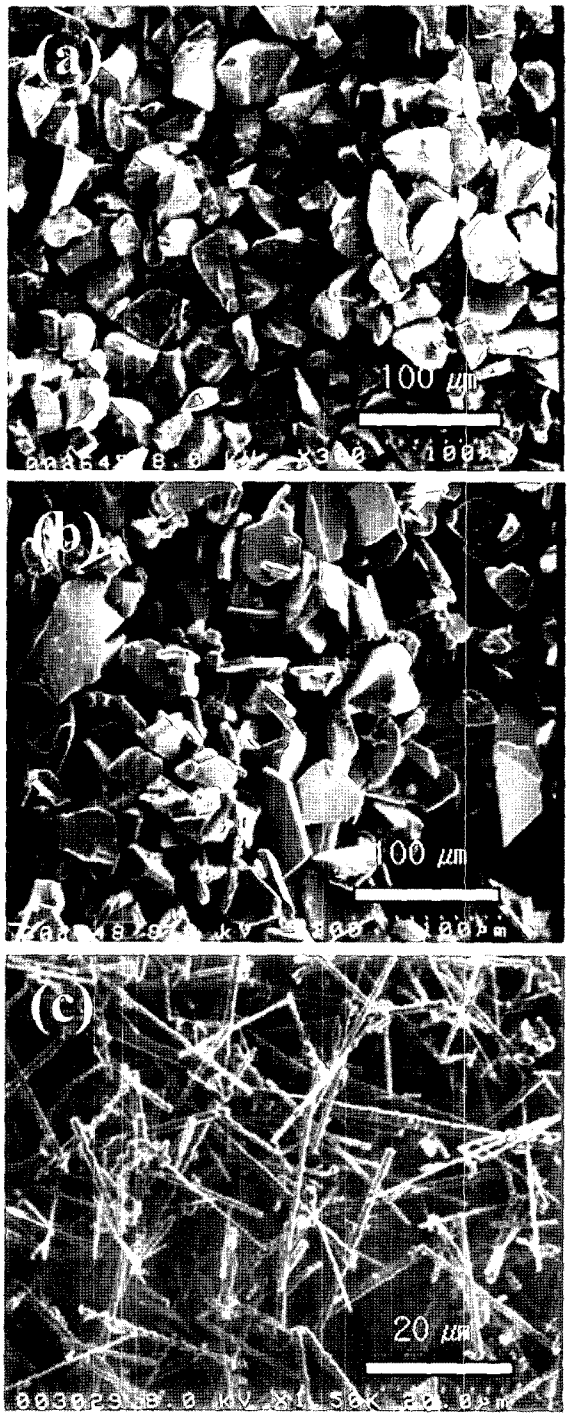

Figure 4. SEM images of silicon carbides used in this study: (a) particulate SiC; (b) platelet SiC; (c) whisker type SiC.

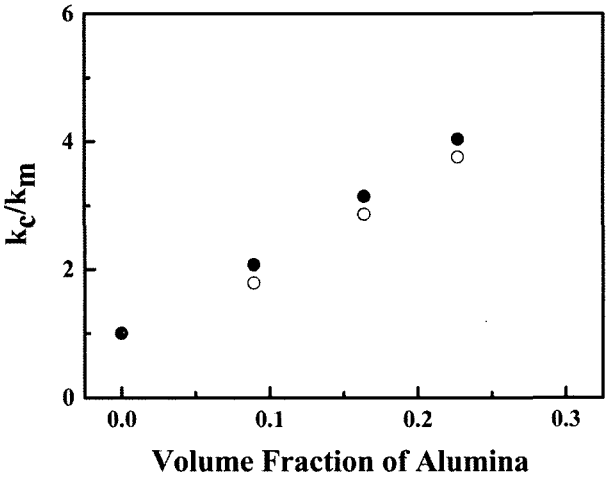

Figure 5. The change of k_c/k_m for EHAO resin with the various amounts of 86.7 μm alumina without (○) and with the treatment (●) by GPS coupling agent.

molar ratio up to 1.05, after which it decreased dramatically with increasing molar ratio. According to the results given in Figure 7, we chose two different values (1.05 and 1.22) of the molar ratios of crosslinking agent to EHAO resin.

Figure 7 shows the change of probe tack and peel strength of a composite consisting of EHAO resin with various amounts of alumina as a function of the diameter of alumina. Here, the molar ratio crosslinking agent was 1.22. With increasing content of alumina, the probe tack decreased gradually. However, peel strength of a composite with alumina having greater than 0.1 volume fraction decreased sharply and exhibited lower values (less than 50 N/m) which cannot be used for conductive adhesives. A sharp decrease in peel strength is attributed to the poor wetting on the glass substrate resulting from the increase of the modulus of the composite. On the other hand, probe tack decreased gradually with increasing amounts of alumina. The different behavior might be due to different test modes: sliding (or shear) force

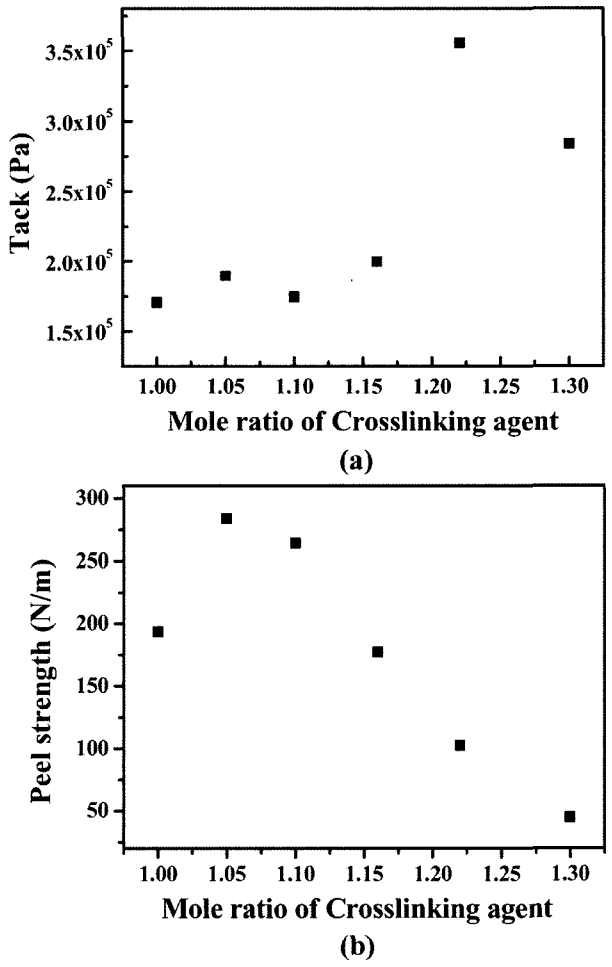

Figure 6. Probe tack (a) and peel strength (b) of EHAO resin itself after crosslinking at various molar ratios of crosslinking agent to EHAO.

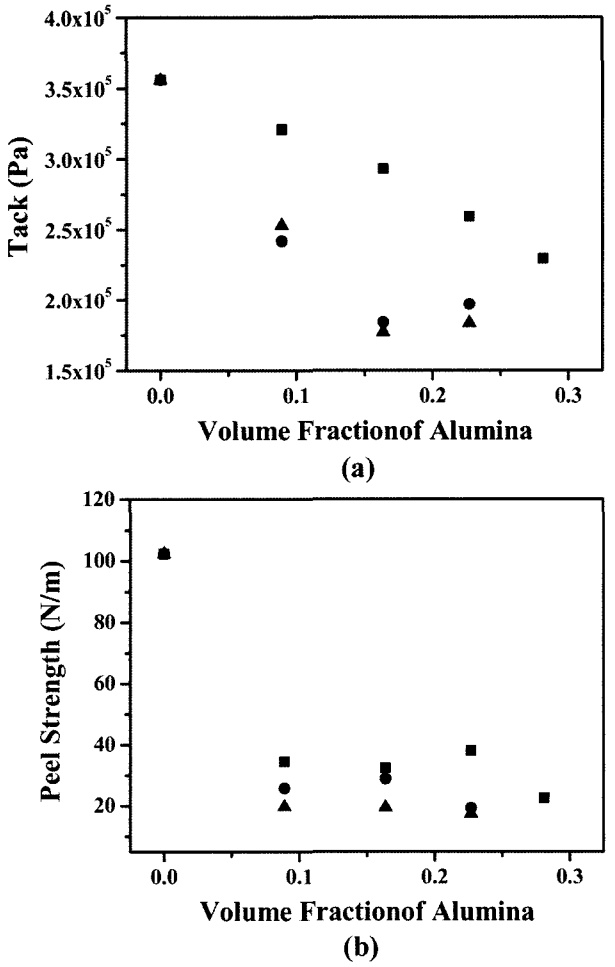

Figure 7. Probe tack (a) and peel strength (b) for EHAO resin with various amounts of alumina as a function of particle diameter: 5.9 μm (■); 43.9 μm (●); 86.7 μm (▲). The molar ratio of crosslinking agent to EHAO was 1.22.

for peel test versus normal force for probe tack.

Figure 8 shows the change of probe tack and peel strength of a composite consisting of EHAO resin with various amounts of alumina at a molar ratio of crosslinking agent of 1.05. Even though probe tack of neat resin was smaller than that at a molar ratio of 1.22, the higher tack properties were obtained with increasing the amounts of alumina. This indicated that the lower modulus of EHAO resin at a molar ratio of 1.05 increased with increasing amount of alumina. Peel strength of a composite with the smallest alumina particles (5.9 μm) decreased gradually with increasing amount of particles, whereas that for other two composites with larger particle sizes decreased dramatically. However, we found that when the molar ratio was smaller than 1.0, cohesive failure occurred; thus, residues were observed on the glass substrate. Furthermore, as shown in Figure 1, k_c of a composite with the smallest particle size of alumina was smaller than that with larger sized particles.

In order to increase peel strength, we employed UV-curable IRR84 resin. Figure 9 shows that peel strength and tack of IRR84 resin with alumina were much larger than those of EHAO resin. Especially, even for a composite with the largest particle size of alumina (86.7 μm), a composite having a volume fraction of 0.22 exhibited a relatively high peel strength (~200 N/m). A large peel strength compared with EHAO resin system is due to the difference of polarity of acrylic acid in IRR84 as well as uniform particle dispersion in the resin resulting from shorter crosslinking time (30 min for UV-curing versus a week for thermal crosslinking). Figure 10 shows the changes of k_c/k_m with volume fraction of alumina particle with 86.7 μm. k_c/k_m increased with increasing volume fraction of the alumina. Also, the rate of increase of k_c/k_m for IRR84 resin was higher than that for EHAO resin (see Figure 1). This is due to uniform particle dispersion in the resin because of shorter curing time compared with thermal curing. We found that conductive particles sometimes sink to the bottom of the adhesive layer for longer curing time, which reduces the thermal conductivity. However, the k_m of IRR84 resin itself was 0.286 W/mK,

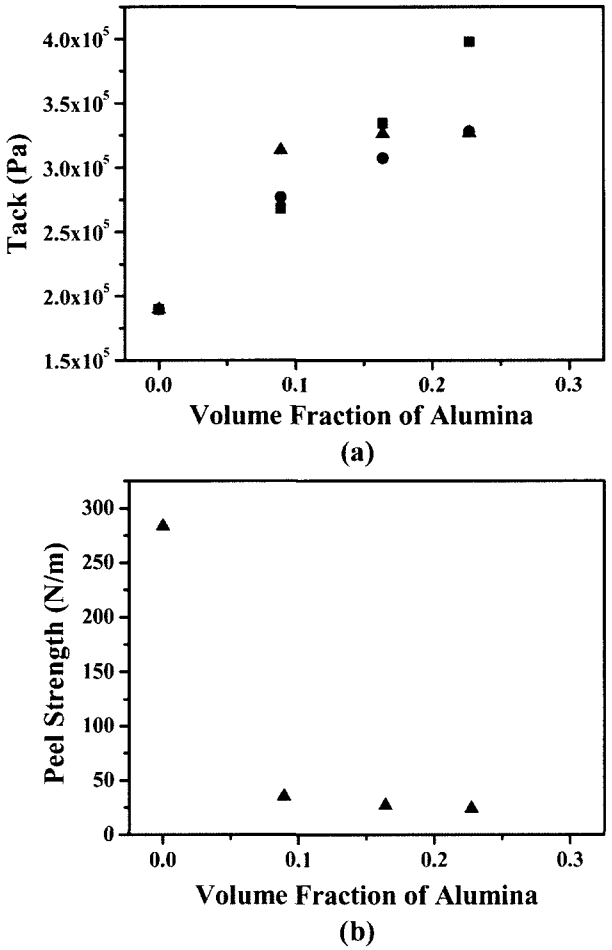

Figure 8. Probe tack (a) and peel strength (b) for EHAO resin with various amounts of alumina with three different particles sizes: 5.9 μm (■); 43.9 μm (●); 86.7 μm (▲). The molar ratio of crosslinking agent to EHAO was 1.05.

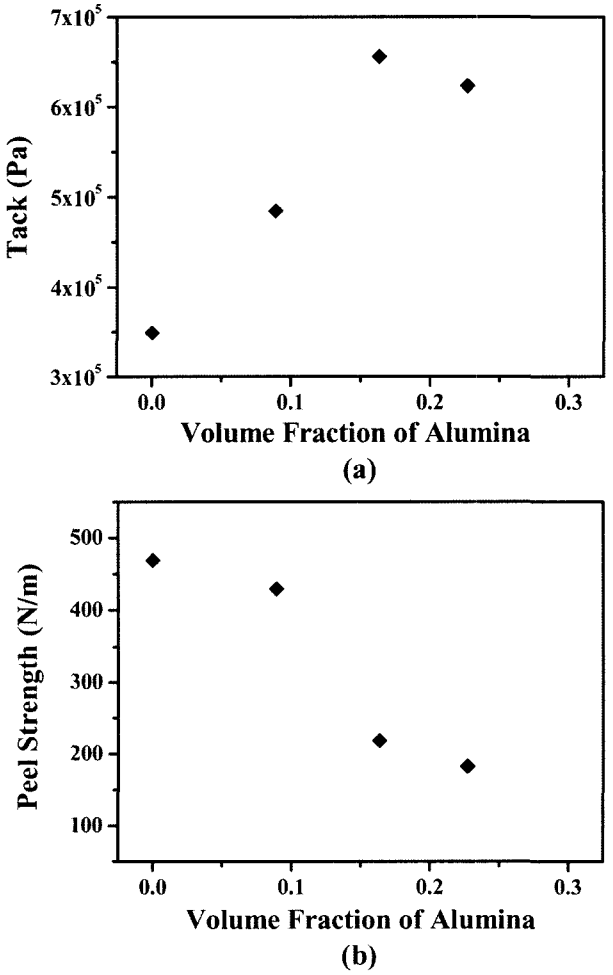

Figure 9. Probe tack (a) and peel strength (b) for IRR84 resin with various amounts of 86.7 μm alumina.

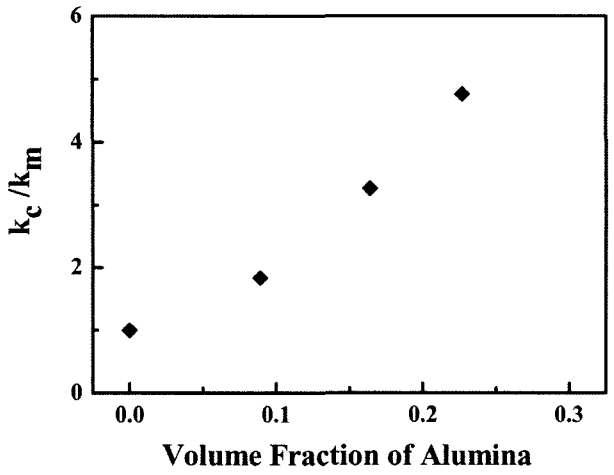

Figure 10. k_c/k_m for IRR84 resin with various amounts of 86.7 μm alumina.

which is smaller than that (0.428 W/mK) of EHAO resin. Thus, the actual value of k_c of IRR84 resin with alumina particles was lower than that of EHAO resin.

Conclusions

We have shown that the shape and size of conductive particles profoundly affected k for thermally conductive pressure-sensitive adhesives. At a given volume fraction of particles, k increased with increasing both the diameter and the aspect ratio of the particles. This is due to the smaller interfacial thermal barrier at the interface between the particles and the matrix, and the easy pathway among particles, respectively. We have also shown that the use of a coupling agent is an effective means to increasing the k of the composite.

However, thermally crosslinkable EHAO resin with particles exhibited very poor peel strength to be employed for commercial purposes. Instead, UV curable resin with larger amounts of particles (thus higher k) exhibited good tack and peel strength.

Acknowledgements. This work was supported by the National Creative Research Initiative Program supported by KOSEF.

References

(1) H. Ishida and S. Rimdusit, *Thermochimica Acta*, **320**, 177 (1998).
(2) J. Bae, W. Kim, and S. Cho, *J. Material Science*, **35**, 5907 (2000).
(3) Y. Xu, D. D. L. Chung, and C. Mroz, *Composites: Part A*, **32**, 1749 (2001).
(4) P. Bujard, G. Kuhnlein, S. Ino, and T. Shiobara, *IEEE Transac. Compn. Packg. Manu. Tech: Part A*, **17**, 527 (1994).
(5) R. F. Hill and P. H. Supancic, *J. Am. Ceram. Soc.*, **85**, 851 (2002).
(6) C. T. Murrary, R. L. Rudman, M. B. Sabade, and A. V. Pocius, *MRS Bulletin*, **28**, 449 (2003).
(7) Japan Patent, 2000-290615A (Tokai Rubber Co., Japan).
(8) Japan Patent 2005-97440A (Sumitio-3M Co., Japan).
(9) J. W. Bae, W. Kim, S. Hwang, Y. S. Choe, and S. H. Lee, *Macromol. Res.*, **12**, 78 (2004).
(10) D. W. Kang and H. G. Yeo, *Polymer(Korea)*, **29**, 161 (2005).
(11) C. P. Wong and R. S. Bollampally, *J. Appl. Polym. Sci.*, **74**, 3396 (1999).
(12) C. P. Wong and R. S. Bollampally, *IEEE Transac. Adv. Packg.*, **22**, 54 (1999).
(13) I. H. Tavman, *Int. Comm. Heat Mass Transfer*, **25**, 723 (1998).
(14) Y. Nagai and G. Lai, *J. Ceram. Soc. of Japan*, **105**, 213 (1996).
(15) Y. P. Mamunya, V. V. Davydenko, P. Pissis, and E. V. Lebedev, *Eur. Polym. J.*, **38**, 1887 (2002).
(16) D. Kumluţş, İ. H. Tavman, and M. T. Çoban, *Composites Sci. Technol.*, **63**, 113 (2003).
(17) A. Boudenne, L. Ibos, M. Fois, J. C. Majesté, and E. Géhin, *Composites: Part A*, **36**, 1545 (2005).
(18) S. E. Gustafsson, *Rev. Sci. Instrum.*, **62**, 797 (1991).
(19) J. K. Kim, W. H. Kim, and D. H. Lee, *Polymer*, **43**, 5005 (2002).