

Fabrication of acrylic copolymer with aluminum nitride fillers and its physical and thermal properties

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Abstract—Heat dissipation during operations of electronic devices is a serious issue with device miniaturization and high power consumption. As one practical approach to reducing the device temperature, thermally conductive adhesives can be used between printed circuit board and heatsink materials. By incorporating the aluminum nitride (AlN) with acrylic copolymer matrix, thermal conductivity and adhesive properties are examined with different sizes and content of particulate fillers. Acrylic copolymer is synthesized using butyl acrylate and acrylic acid monomers via solution polymerization, and AlN particles are used as thermally conductive fillers. The overall monomer conversion reaches more than 96% after 140 min reaction time. Considering both adhesive properties and thermal conductivity of adhesives, it is desirable to apply 20 wt% nano-AlN filler to acrylic copolymer adhesives.

Keywords: Thermal Conductivity, Adhesive, Adhesion, Polymers, Composites

INTRODUCTION

Recent trends in the development of electronic devices include miniaturization and high power consumption, since most device applications require convenient portability with good functional performance. However, this change in devices generates a large amount of heat, which negatively affects life span and reliability. Thus, it is important to develop methods for effective heat dissipation from devices to surroundings [1]. Although there are several heat dissipation methods using pads, sheets, and tapes, thermally conductive adhesives have been widely used because of ease of use and low price [2].

Thermally conductive adhesive is generally composed of polymer matrix and conductive particles, and it is usually a type of viscoelastic material that can interlock surfaces with light contact pressure and short contact time [3]. Acrylic resins have been widely used in adhesive industries because of outstanding adhesive properties, transparency, and low toxicity [3,4]. Generally, acrylic adhesives have good wettability to surfaces due to high chain mobility at room temperature ($\geq T_g$), but the low T_g adhesives cannot provide enough shear force to prevent the adhesives from cohesive failures. Therefore, acrylic adhesives often include some fractions of high T_g materials to withstand from failures [5]. In addition, cohesion of adhesive materials and their wettability to substrates are strongly related to the adhesive properties. In case of strong wettability, adhesive materials can be broken from substrates under detaching mechanism, and adhesive materials with high cohesive strength cannot easily permeate into the substrates. Therefore, it leads to reduction in real contact area to substrates with low adhesive properties. Most fillers in polymer matrix act as a reinforcing

agent for cohesion, and some studies showed the increase of adhesive properties with increasing filler contents. However, adhesive properties eventually decrease after the optimal amount of filler [6,7]. Since acrylic polymers have very low thermal conductivity, various conductive particles such as zinc oxide, aluminum nitride, boron nitride, and magnesium oxide are reported for uses [8,9]. These particles not only have high thermal conductivity but also electric insulation for preventing electrical shortages, because thermally conductive adhesives are often used for bonding between heat sink and printed circuit board.

Some studies also reported filler concentration higher than 50 wt% for thermally conductive polymers [1,10], but it can be problematic in achieving good adhesive properties. Thus, it is important to balance both thermal conductivity and adhesive properties. In this study, we fabricated thermally conductive adhesives using butyl acrylate/acrylic acid copolymer and aluminum nitride particles. The monomer conversion was examined as a function of reaction time by Fourier transformed infrared spectroscopy (FTIR Frontier, PerkinElmer Inc.), and the effects of particle sizes on thermal conductivity and adhesive properties were investigated for manufacturing well-balanced thermally conductive adhesives.

EXPERIMENTAL

1. Materials

Butyl acrylate (BA, 99% purity, Sigma-Aldrich), acrylic acid anhydrous (AA, 99% purity, Sigma-Aldrich), ethyl acetate anhydrous (EA, 99.8% purity, Sigma-Aldrich), 2, 2'-azobisisobutyronitrile (AIBN, 98% purity, Junsei Chemical), nano-aluminum nitride (nano-AlN, <100 nm, Sigma-Aldrich), micro-aluminum nitride (micro-AlN, 1–2 μ m, Hansong global, 99.5% purity) were purchased and used without further purification in polymerization reactions.

2. Synthesis

Solution polymerization for the thermally conductive adhesives

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Table 1. Formulations details for thermally conductive adhesives

Sample	BA (g)	AA (g)	AlN (g)
M1	36.86	1.14	2.00
M2	34.92	1.08	4.00
M3	32.98	1.02	6.00
M4	31.04	0.96	8.00
M5	29.10	0.90	10.00
N1	36.86	1.14	2.00
N2	34.92	1.08	4.00
N3	32.98	1.02	6.00
N4	31.04	0.96	8.00
N5	29.10	0.90	10.00

was performed in EA solvent medium. Table 1 shows formulation details for copolymer composition and filler contents at fixed solvent amount. According to our previous study, well-balanced adhesive properties were obtained at the monomer ratio (BA : AA) of 97 : 3, and thus initial monomer ratio was fixed at 97 : 3 in this study [11]. The AIBN initiator was included in the reaction medium at 0.1 wt%. The polymerization reactions were conducted in a four-necked reactor equipped with N₂ gas inlet, condenser, thermometer, and mechanical stirrer. After the reactor was purged with N₂ gas for 5 min, the solution was continuously stirred at 250 rpm during heating the reactor at 80 °C for 3 h. Then, the synthesized polymer solutions were cooled to room temperature. The M and N series represent adhesive materials including micro- and nano-AlN fillers.

3. Tape Preparation

Thermally conductive adhesives consist of corona-treated polyester films (50 µm, SKC), an adhesive layer, and Si-treated polyester films (23 µm, SKC). The corona-treated film was fixed on the bar coater, and then the synthesized solution was poured on the fixed film. The solution was cast with the #22 wire-rod at 30 cm/min. The cast samples were dried in a convection oven at 70 °C for 10 min, and the dried adhesive layer was protected by Si-treated polyester film.

4. Monomer Conversion

Samples of the polymer solution were taken from the reactor every 20 minutes using syringes and stored in vials. To terminate the polymerization, the samples were cooled in ice-water bath for 20 minutes. Then, FTIR with an attenuated total reflectance (ATR) accessory was used to examine the monomer conversion from the C=C bonding analysis. Since the monomer concentration is proportional to peak heights of FTIR spectra as reported by Chatizi et al. [12], monomer conversion (x) can be calculated using the following equation:

$$x(\text{mol}\%) = 1 - \frac{\text{peak height at time } t}{\text{peak height at time } t=0} \quad (1)$$

5. Adhesive Characterization

Tack and peel forces were measured by the universal test machine (LS1, LLOYD). The specimen for peel force was cut into 25 mm width and 200 mm length, and the samples were attached to stainless steel substrate. After the attached samples were pressed twice

using 2 kg rubber roller, they were kept for 10 minutes at room temperature. The measurements were conducted at 180° between the stainless steels and samples with a crosshead speed of 300 mm/min, and the average value from three measurements was recorded. The tack force was measured using a stainless steel cylindrical probe of 5 mm diameter. The rate of probe approach to the samples was 20 mm/min, and the initial operating pressure was 1,000 kg/m² for 1 sec. The average tack force was obtained from three different measurements at 300 mm/min detaching speed. Surface of the acrylic adhesive with micro- and nano-AlN was measured by scanning electron microscopy (SNE-3000M, SEC Co. Ltd.) at an acceleration voltage of 15 kV. Thermal conductivity of samples can be measured as the products of the thermal diffusivity (δ mm²/s), specific heat (C , J/g·K), and bulk density (ρ g/cm³) [13]. The thermal diffusivity of samples was measured by laser flash method (LFA 447, NETZSCH) at 25 °C. The specific heat and bulk density of samples were measured by differential scanning calorimetry (DSC 8000, PerkinElmer Inc.) and Archimedes method, respectively. The scanning temperature of DSC was ranged from −70 °C to 70 °C at 20 °C/min scan rate.

RESULTS AND DISCUSSION

Conversion of monomers during polymerization can be examined with the strong FTIR peaks from monomers. A typical representative peak from both BA and AA monomers appears at 1,635 cm^{−1} as a stretch vibration mode of the carbon double bond as shown in Figs. 1(a) and 1(b) [14]. Additional peaks are shown at 1,409 cm^{−1} (=CH₂ vibrational deformation from BA, O-H bending from AA) and at 974 cm^{−1} (=CH₂ wagging from BA, =CH₂ stretch vibration from AA), and thus these peaks cannot be used as a reference peak because of the skewed contributions from both monomers. Fig. 1(c) shows a spectrum of pure solvent EA with no peak at 1,635 cm^{−1}, so the intensity of absorbance peak (1,635 cm^{−1}) can be utilized in measuring monomer conversion. Fig. 1(d) shows the monomer conversion as a function of reaction time with and without AlN fillers. Regardless of the AlN content, the conversion reached over 90% after 80 min reaction. It gradually increased to 96%, and no further increment was observed after 140 min. Therefore, the polymer solution could be considered as a stable condition after 140 min reaction time in polymerization.

Viscoelasticity of adhesive materials and their wettability on substrates are strongly related to the adhesive properties, such as tack and peel force. Fig. 2 shows the tack and peel force as a function of AlN content for both micro- and nano-particles. The tack force decreased with increasing the AlN content, but it showed less decreasing tendency with the nano-filler than the micro-filler case. In addition, the peel force showed also decreasing tendency with increasing the filler content, but its reduction in micro-filler case was much sharper than that in nano-filler case. As shown in Fig. 2(b), the peel force is similar for both nano- and micro-AlN cases at the filler content lower than 10 wt%, but it shows higher reduction in micro-filler case with higher filler content. In addition, the micro-AlN filled sample was observed as adhesive failure mechanism between the substrate and adhesive layer, whereas the nano-AlN filled sample showed cohesive failure behavior. This differ-

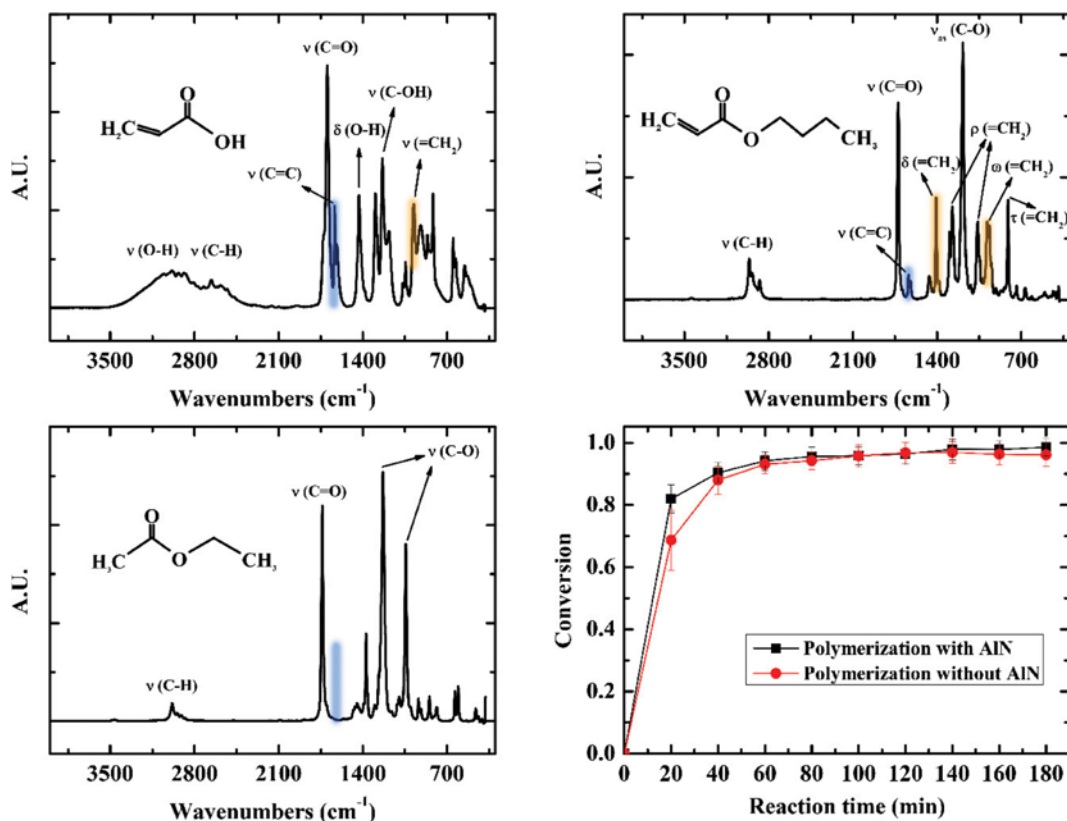


Fig. 1. FTIR-ATR spectra of (a) acrylic acid, (b) butyl acrylate, (c) ethyl acetate anhydrous, and (d) overall monomer conversion.

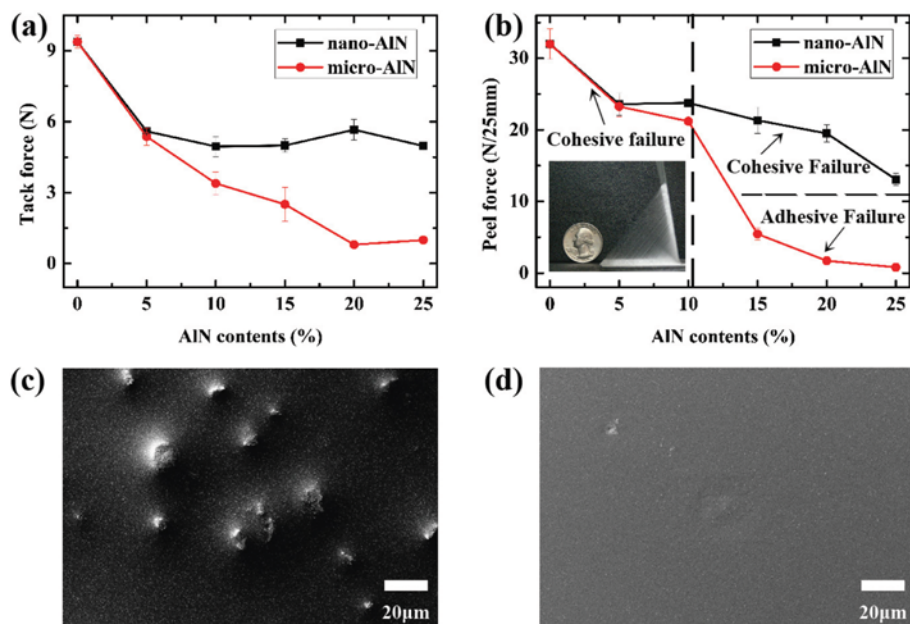


Fig. 2. Tack (a) and peel (b) forces of adhesive materials as a function of AlN content, and SEM images of surface of adhesives at 15 wt% with micro- (c) and nano-AlN (d).

ence is mainly attributed to the wettability of adhesive layer to the substrate depending on the particle size and content of particles included in the adhesive layers. In addition, the increase in wettability enhanced mechanical interlocking and anchoring the adhe-

sive with pores and irregularities on the substrate. Figs 2(c) and 2(d) show SEM images for the adhesive surfaces adhering to the substrates from micro-AlN and nano-AlN filler cases. The adhesive with the micro-AlN filler revealed higher number of particles

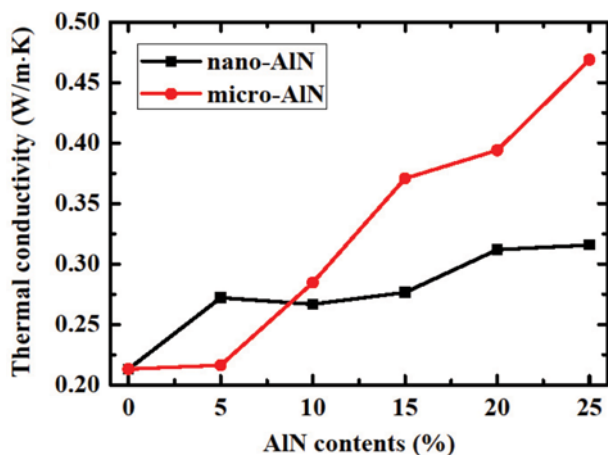


Fig. 3. Thermal conductivity of composite adhesives as a function of AlN contents.

at the surface than with the nano-AlN filler, which can further lead to low adhesive properties with micro-AlN filler. Therefore, based on the observations of surface morphology and adhesive properties, acrylic adhesives are recommended to have less than 20 wt% nano- and 10 wt% micro-AlN fillers for desirable characteristics of adhesives.

For commercial applications of thermally conductive adhesives, thermal conductivity is an important characteristic of products. Fig. 3 shows the thermal conductivity as a function of AlN content for two different particle sizes. Regardless of the particle sizes, the thermal conductivity increased with increasing the AlN fillers. It is possibly due to the increased heat transfer of the adhesives by inclusions of particles in polymer matrix [15,16]. As shown in Fig. 3, however, the increasing tendency of thermal conductivity with the micro-AlN is sharper than that with nano-AlN because nano-sized particles have higher surface contact area with polymer matrix than micro-sized particles [9]. The presence of the interfacial thermal barrier resistance always diminishes the efficiency of the thermal conduction [17]. Therefore, adhesives with nano-fillers have more interfacial thermal barrier than with micro-fillers, and thus thermal conductivity reveals less increment with nano-filler than with micrometer filler in the composite adhesives.

CONCLUSIONS

Thermally conductive adhesives, including nano- and micro-AlN fillers at various filler content, were prepared by copolymerization of butyl acrylate and acrylic acid monomers. The conversion of monomers reached over 90% after 80 min reaction time

regardless of filler inclusions. Both tack and peel force decreased with increasing the filler content, and it is recommended to have less than 20 wt% nano- and 10 wt% micro-AlN fillers for desirable adhesive characteristics. Thermal conductivity of adhesives increased with increasing AlN filler content. Considering both adhesive properties and thermal conductivity for thermally conductive adhesives, it is desirable to apply 20 wt% nano-AlN filler to acrylic copolymer adhesives.

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