Effects of composition and layer thickness of a butyl acrylate/acrylic acid copolymer on the adhesion properties

Deoukchen Ghim and Jung Hyeun Kim[†]

Department of Chemical Engineering, University of Seoul, 163, Siripdae-ro, Dongdaemun-gu, Seoul 130-743, Korea
(*Received 13 April 2015 • accepted 8 July 2015*)

Abstract−Acrylic pressure-sensitive adhesives are synthesized by solution copolymerization using n-butyl acrylate and acrylic acid (AA) in ethyl acetate anhydrous. The copolymer composition is controlled for good adhesive properties by varying AA content. The monomer conversion is measured by the gravimetric method and FTIR technique. The adhesive layer thickness is measured by scanning electron microscopy, and the adhesive properties are evaluated with loop tack, 180° peel, and holding time measurements. The peel force increases with increasing the AA content up to 3 wt% and decreases at the AA content higher than 3 wt%, but the tack force decreases with increasing the AA content. The holding time increases with increasing the AA content, and it shows a similar trend with the T_g of adhesives. The increase of layer thickness improves tack and peel forces, but it weakens the holding power. A tape thickness of about 20 μm shows well-balanced properties at 3 wt% AA content in the acrylic copolymer system.

Keywords: Solution Synthesis, Adhesion, Polymers

INTRODUCTION

Pressure-sensitive adhesive (PSA) is usually a viscoelastic material that can semipermanently bond to solid surfaces under light contact pressure and short contact time [1]. The PSA is commonly used as tapes, labels, and protective films which are applied in various fields ranging from simple applications (e.g., self-adhesive envelops, sticky note) to industrial products (e.g., light emitting diode packages, automotive, and bioelectrodes) [2,3]. Amongst the PSA materials, the acrylic system is very popular due to outstanding adhesive properties, resistant to oxidation, transparent, thermal stability and anti-aging against solar irradiation [4-7]. Usually, low glass transition temperature (T_g) is favorable for tape materials because the wettability of low T_g material is superior to the high T_g material on the substrates. However, the low T_g material itself does not provide enough resistance to the shear force acting on the tape surface. Therefore, a combination of hard components with the soft low T_g base materials is desirable to achieve both wettability from the soft part and material strength from the hard part.

The acrylic PSA is generally synthesized by solution or emulsion polymerization. Among them, solution polymerization is preferred because solvent-borne PSA has high shear strength as well as good peel and tack strength [8]. In the emulsion polymerization, surfactants are used to form micelle structure between water and monomer, and they still remain on the polymer particles as residues after the drying process. Thus, they can weaken the material properties. However, solution polymerization using organic solvents does not contain contaminants, and it leads to high polymer chain compatibility and high shear strength of material.

In this study, we synthesized acrylic PSA through solution polymerization using monomers of n-butyl acrylate and acrylic acid in organic solvent of ethyl acetate anhydrous. The monomer conversion was examined as a function of reaction time by both conventional gravimetric method and FTIR-ATR technique, and the effects of copolymer composition and adhesive layer thickness on the tape characteristics were investigated for well-balanced adhesive properties. There are three major differences from the other previously reported articles. First, effects of monomer composition and thickness of adhesive layer on the adhesive properties are investigated for the butyl acrylate/acrylic acid copolymer in solution polymerization. Secondly, detachment mechanism of the adhesive layer is analyzed with the monomer composition. Lastly, the SEM and optical images are used not only to measure the thickness of adhesive layer but also to check the cohesive failure phenomenon.

EXPERIMENTAL

1. Methods

Butyl acrylate (BA, 99% purity, Sigma-Aldrich), acrylic acid anhydrous (AA, 99% purity, Sigma-Aldrich), ethyl acetate anhydrous (EA, 99.8% purity, Sigma-Aldrich), and 2, 2′-azobisiso-butyronitrile (AIBN, 98% purity, Junsei Chemical) were purchased and used without further purification in polymerization reactions. Acrylic polymer adhesives were synthesized by solution polymerization with 40 wt% monomer concentrations in the 60 wt% EA solvent medium. The monomer ratios (BA : AA) ranged from 100 : 0 to 91 : 9 in 40 wt% concentration, and the AIBN initiator was included in the reaction medium at the beginning. The polymerization reactions were in a four-necked reactor equipped with N_2 gas inlet, condenser, thermometer, and mechanical stirrer. After the reactor was purged with N_2 gas for 5 min, the solution was continuously stirred at 250 rpm during heating and keeping the reactor at 80 °C for 3 h. Then,

[†]To whom correspondence should be addressed.
E-mail: jhkimad@uos.ac.kr

the synthesized polymer solutions were cooled to room temperature for casting adhesives.

In casting the adhesive layer, the corona-treated (50 μm, SKC) and silicone-treated (23 μm, SKC) polyester films were used. In manufacturing the adhesive layer, various wire-rod numbers of 6, 14, 22, 30, and 38 were chosen to give dry layer thickness up to 35 μm. The samples consisting of a corona-treated film, an adhesive layer, and a silicon-treated film were fabricated to examine adhesive properties. The corona-treated polyester films were fixed on the coater, and then the polymer solution was poured on the film. The solution was evenly cast with a selected wire-rod at 30 cm/min, and the cast samples were dried at 70 °C for 10 min. Finally, the dried adhesive layers were covered with the Si-treated films for protection.

2. Characterization

Thickness of the acrylic adhesive layer coated on PET film was measured by scanning electron microscopy (SNE-3000M, SEC Co. Ltd.) at an acceleration voltage of 30 kV. Glass transition temperatures of the adhesives were determined by differential scanning calorimetry (DSC 8000, PerkinElmer Inc.); the scanning temperature ranged from −70 °C to 70 °C at 20 °C/min. Monomer conversions were calculated by a conventional gravimetric method [9]. Fourier-transform infrared spectroscopy (FT-IR Frontier, PerkinElmer Inc.) with an attenuated total reflectance (ATR) accessory was also used to qualitatively examine the monomer conversion from the C=C bonding analysis. Loop tack and 180° peel tests were performed by the universal test machine (Instron5565, Instron Inc.) with 25 mm×200 mm samples, and the holding power test with a 1 kg weight was conducted on the 25 mm×25 mm area [10].

RESULTS AND DISCUSSION

The thickness of the adhesive layer was measured with the SEM images, and Table 1 shows the results of measured thicknesses and predictions. As expected, the layer thickness increases linearly with increasing the wire-rod number.

Fig. 1 shows the monomer conversion as a function of reaction time by averaging the conversions from the various monomer compositions. The conversion reached about 90% after 60 min reaction regardless of the monomer ratios. It gradually increased to 96%, and no further increment was observed after 100 min. In addition, the peak height of the C=C bond was also monitored by ATR-FTIR at 97 : 3 (BA : AA). The inset plot shows the strong characteristic wavenumber contributed from C=C bond at 1,408 cm^{-1} [11]. The decrease in peak height was noted as polymerization proceeded, and it could be due to the reduction of the C=C bonds in the solution by polymerization. This FTIR characteristic peak also shows a similar trend with the gravimetric method, and it did not show large
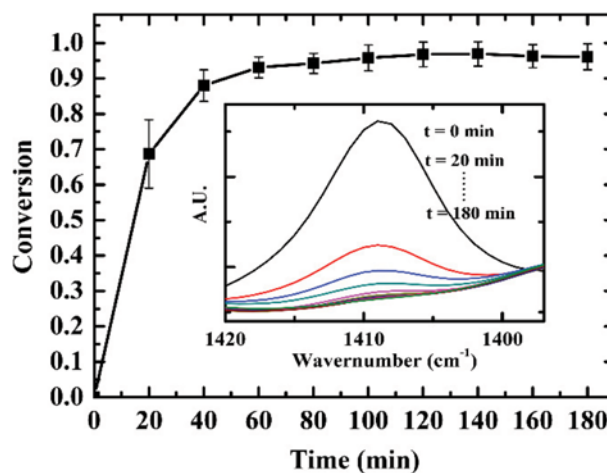

Fig. 1. Monomer conversion by a gravimetric method, and the inset showing changes of peak height at 1,408 cm^{-1} indicating the presence of C=C bonds.

change after 100 min. Therefore, the polymer solution could be considered as a stable condition after 100 min for preparations of adhesive layers.

Adhesion properties are composed of peel force, tack force, and holding power. Fig. 2(a) shows the peel and tack forces measured with the 20 μm adhesive layer. The tack force measured with a glass substrate decreased with increasing the AA content. However, the peel force showed a maximum value at 3 wt% AA content. Generally, the peel strength is related to viscoelastic properties of the adhesive such as interfacial adhesion and cohesive failure. In this respect, the adhesive material strength increases with increasing the AA content, whereas the interfacial adhesion decreases with increasing the AA content. In addition, cohesive failure of the adhesive layer was observed at an AA content lower than 3 wt%. Therefore, there is an optimum composition for the highest peel strength for this copolymer system. Fig. 2(b) shows the failure time related to the holding power of the adhesives and T_g for the same samples. Shear resistance is also proportional to the strength of the adhesive layer, and it shows a similar trend with the copolymer T_g. Therefore, the acrylic copolymer adhesive with 3 wt% AA content is the optimum composition for balanced adhesive properties.

At this copolymer composition, the layer thickness was varied as an adhesive parameter up to 35 μm. Fig. 3(a) shows the increments of both peel and tack forces with increasing the layer thickness, but Fig. 3(b) shows lower holding time at higher layer thickness. Peel and tack forces are enhanced as the thickness of the adhesive layer increases because a larger volume of adhesive layer can dissipate more energy during the force measurements, and it causes a

Table 1. Predicted and measured thicknesses of the acrylic adhesive layers

Wire-rod #	6	14	22	30	38
Predicted* thickness (μm)	5.5	12.8	20.1	27.4	34.8
Measured thickness (μm)	4.8±0.5	12.3±0.2	20.2±0.7	28.1±0.2	35.1±0.6

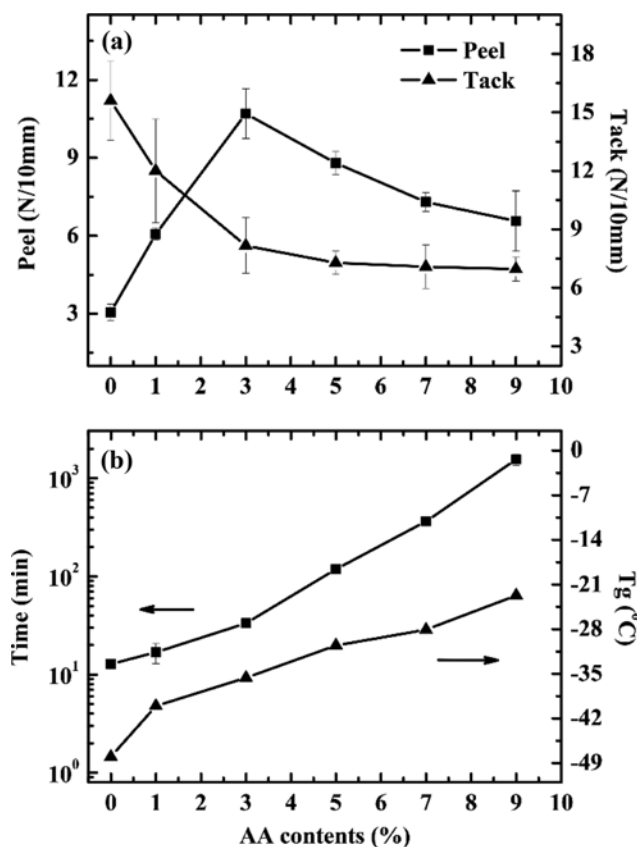*Prediction: thickness from the wire-rod number×solid contents in the polymer solution

Fig. 2. Adhesive properties: (a) Peel and tack forces, (b) holding time and glass transition temperature (T_g).

Fig. 3. Adhesive properties at 3 wt% AA content: (a) Peel and tack forces, (b) holding time, and detached tape images from 20 μm (c) and 27 μm (d).

rise of total work [12]. However, the holding power is inversely proportional to the adhesive layer thickness because the deformation of the thick adhesive layer is relatively easier than that of the thin case [8]. In addition, the surface-to-volume ratio of the adhesive layer decreases with increasing the layer thickness, and so the time to failure of the adhesive layer decreases as the layer thickness increases. Fig. 3(c) and 3(d) show photographs of the peeled tapes from 20 μm and 27 μm, respectively. Fig. 3(c) represents a clean detachment case, and it is desirable in various tape applications. However, Fig. 3(d) shows cohesive failure phenomenon of the adhesive layer, and it is difficult to use as tapes. Therefore, the most recommendable thickness of the adhesive layer with well-balanced tape properties is about 20 μm.

CONCLUSIONS

Acrylic adhesives were synthesized by varying AA content in the butyl acrylate and acrylic acid monomer mixture. The peel force increased with increasing the AA content up to 3 wt%, but it decreased at the AA content higher than 3 wt%. The tack force decreased with increasing the AA content due to the reduced wettability of the adhesive layer, and the holding time was linearly increased with increasing the AA content. The thickness of the adhesive layer changed the adhesive properties, and the thicker layer showed higher tack and peel forces but lower holding power. Therefore, the thickness of the acrylic copolymer adhesive is an important parameter
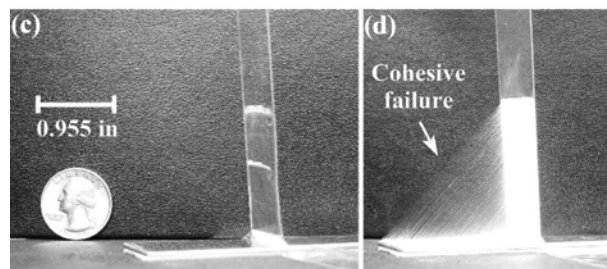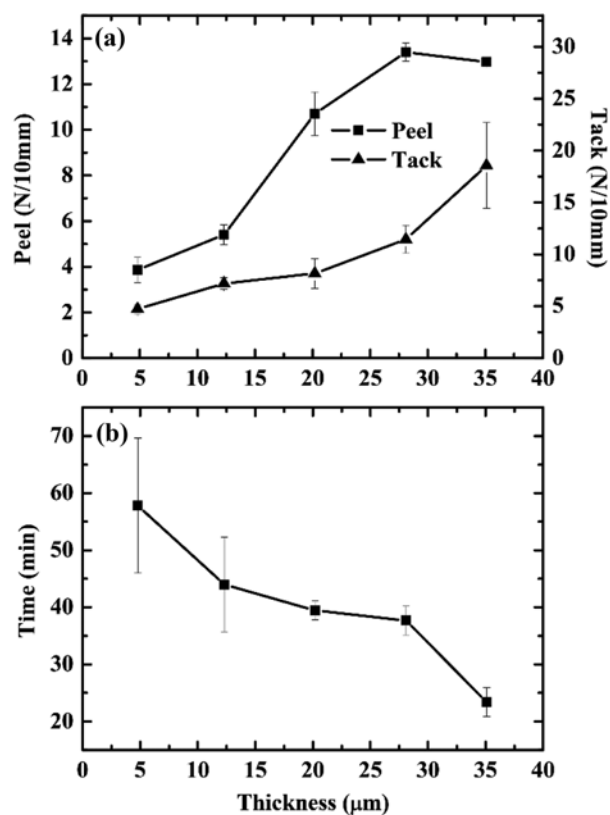
for well-balanced tape properties, and it was about 20 μm for the optimum properties at 3 wt% of AA content in the acrylic copolymer system.

REFERENCES

1. A. Agirre, J. Nase, E. Degrandi, C. Creton and J. M. Asua, *Macromolecules*, **43**, 8924 (2010).
2. S. Sun, M. Li and A. Liu, *Int. J. Adhes. Adhes.*, **41**, 98 (2013).
3. H. Shen, J. Zhang, S. Liu, G. Liu, L. Zhang and X. Qu, *J. Appl. Polym. Sci.*, **107**, 1793 (2008).

4. X. Jin, Y. Bai, L. Shao, B. Yang and Y. Tang, *Express Polym. Lett.*, **3**, 814 (2009).
5. Z. Czech, W. Arabczyk, A. Hełminiak and A. Kowalczyk, *Int. J. Adhes. Adhes.*, **40**, 210 (2013).
6. G. Hui, W. Huang, Y. Song, D. Chen and A. Zhong, *Korean J. Chem. Eng.*, **30**, 1609 (2013).
7. M. Sultan, H. N. Bhatti, M. Zuber and M. Barikani, *Korean J. Chem. Eng.*, **30**, 488 (2013).
8. S. D. Tobing and A. Klein, *J. Appl. Polym. Sci.*, **79**, 2230 (2001).
9. M. Moghbeli, S. Zamir and B. Molaee, *J. Appl. Polym. Sci.*, **108**, 606 (2008).
10. F. Mumtaz, M. Zuber, K. M. Zia, T. Jamil and R. Hussain, *Korean J. Chem. Eng.*, **30**, 2259 (2013).
11. J. Kajtna and U. Šebenik, *Int. J. Adhes. Adhes.*, **29**, 543 (2009).
12. T. Igarashi, *J. Polym. Sci.: Polymer Physics Edition*, **13**, 2129 (1975).