International Journal of Adhesion & Adhesives 50 (2014) 93–95

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Enhanced optical properties and thermal stability of optically clear adhesives

Seung-Woo Lee, Ji-Won Park, Cho-Hee Park, Hyun-Joong Kim*

Laboratory of Adhesion & Bio-Composites, Program in Environmental Materials Science, Research Institute for Agriculture & Life Science, Seoul National University, Seoul 151-921, Republic of Korea

ARTICLE INFO

Article history:
Accepted 27 December 2013
Available online 7 January 2014

Keywords:
Acrylic PSAs
Hafnium carboxyethyl acrylate
Optical properties
Thermal stability
Liquid crystal display

ABSTRACT

To improve the optical properties of acrylic pressure-sensitive adhesives (PSAs) for liquid crystal displays (LCDs), hafnium carboxyethyl acrylate (HCA) was introduced as high refractive index material. Also, UV-curing was used to realize rapid crosslinking so as to enhance the degree of thermal stability. A prism coupler, a UV–visible spectrometer and a thermogravimetric analyzer were employed to assess the optical properties and thermal stability. The results show that the refractive index of the acrylic PSAs with HCA increases suitably compared to that of binder acrylic PSAs in the visible wavelength. Also, a substantial effect is shown on the thermal stability in that hafnium carboxyethyl acrylates are crosslinked due to the presence of tetra-functional acrylic groups caused by the rapid UV-curing.

1. Introduction

Pressure-sensitive adhesives (PSAs) have a range of applications in industry, such as medical products, aircraft, space shuttles, electrical devices, optical products and automobiles. Among them, the demand for PSAs in optical films is increasing with the development of liquid crystal displays (LCDs) [1]. LCDs consist of many types of panels with various PSAs employed to fill the spaces between the panels. PSAs are adhesives that attach to a substrate by low-pressure contact, and they do not require reaction processes like common adhesives. PSAs can be peeled from the substrate without failure, which will allow the recycling of the expensive films that make up the display if a defect is found [2].

There are two properties that PSAs should possess before they can be used in optical films. First, the PSA should be optically clear, and it should have a high refractive index that can prevent light reflection as a result of the difference in the refractive index between the film and the adhesive. This property can be achieved through the use of a transmittable acrylic polymer with a high refractive index monomer [3]. Also, it should have high thermal stability. This condition can be achieved by an additional UV-curing process. UV-curing technology has been used in crosslinking pressure-sensitive adhesives (PSAs), owing to its economic and environmental advantages, with none of the disadvantages associated with using a crosslinking agent. UV-curing technology has many advantages on account of its high performance, inexpensive process and due to the low emission of the associated VOCs [4–7].

In this study, in an effort to enhance the optical properties and thermal stability of acrylic PSAs for LCDs, hafnium carboxyethyl acrylate was used as a high refractive index material to realize UV-cured crosslinking.

2. Experimental

2.1. Materials

2-Ehtylhexyl acrylate (2-EHA, Samchun Pure Chemical, Republic of Korea), acrylic acid (AA, Samchun Pure Chemical, Republic of Korea), 2-phenoxy ethyl acrylate (PEA, 90.0% purity, Tokyo Chemical Industry, Japan) and hafnium carboxyethyl acrylate (HCA, Sigma Aldrich, USA) were used as monomers without purification. Table 1 shows the monomer compositions of the acrylic PSAs. Ethyl acetate (EtAc, Samchun Pure Chemical, Republic of Korea) and methanol (MeOH, Samchun Pure Chemical, Republic of Korea) were used as solvents. 2,2′-Azobisisobutyronitrile (AIBN, Junsei Chemical, Japan) was used as the thermal initiator to start the radical polymerization process. 2-Hydroxy-2-methyl-1-phenyl-propane-1-one (Miwon Specialty Chemical, Republic of Korea) was used as the photoinitiator.

2.2. Synthesis of the binders

For the first step, the binders were synthesized using 2-EHA, AA and 2-PEA by means of solution polymerization. Mixtures of monomers were initiated with 1.0 wt% AIBN in ethyl acetate and methanol containing a 40 wt% solid content. Polymerization was performed in a 500 ml four-necked rounded-bottomed flask

* Corresponding author.
E-mail address: hjokim@snu.ac.kr (H.-J. Kim).

0143-7496/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijadhadh.2013.12.029

Table 1
The monomer compositions of the acrylic PSAs.

Optical acrylic PSAs	Acrylic binders			HCA (phr in acrylic binder)
	2-EHA (wt%)	AA (wt%)	2-PEA (wt%)	
HAC-1	70	5	25	0
HAC-2	70	5	25	0.5
HAC-3	70	5	25	1
HAC-4	70	5	25	2

equipped with a mechanical stirrer, a condenser and a thermometer. A mixture of monomers and 50 wt% of the solvent were heated to 70 °C under constant stirring. After an exothermic reaction, a solvent with AIBN was added slowly over periods of 1, 2 and 3 h. Finally, polymerization was terminated by cooling the mixture to room temperature.

2.3. Preparation of the cured acrylic PSAs

UV-curable PSAs were prepared by blending the polymerized binders, a photoinitiator, and HCA monomer. The amounts of HCA monomer were 0.5, 1.0, 2.0 phr of the binder, and the added photoinitiator was 2 phr of the HCA monomer. At room temperature, the mixture was stirred for about 30 min using a mechanical stirrer. The UV-curable polymers were coated on to the polyester films (PET, 50 μm thickness, SKC, South Korea) using a No.18 bar coater (40 μm wet thickness), after which the film were dried at 80 °C for 20 min. The UV-curable PSA films were cured using conveyor belt-type UV-curing equipment with a 100 W pressure mercury lamp (main wavelength: 340 nm). The UV doses that were used in this study were 1000 mJ/cm^2. The UV doses were measured using an IL390C Light Bug UV radiometer (International Light, USA).

2.4. Optical properties

2.4.1. Prism coupler

The refractive indexes of the PSAs coated on the PET film were determined using a prism coupler (Prism Coupler 2010/M, Metricon, USA). The prism and film were joined and the incidence angle of the laser beam was varied. In this way, the refractive index of both the thickness-and plane directions could be measured.

2.4.2. UV–visible spectrometer

A UV–visible spectrometer (Shimadzu UV-1650PC, Japan) was used to measure the transmittance of the acrylic PSAs. The samples coated on the PET film were set on the instrument alongside the control, bare PET film, and the transmittance levels over the wavelength range of, 380–700 nm, were determined.

2.5. Thermal stability

The thermal stability and decomposition profiles of the dual-curable adhesives were measured using a thermogravimetric analyzer (Perkin Elmer Thermogravimetric Pyris1 TGA model). The sample was loaded into a ceramic pan, and heated from 25 °C to 600 °C at a constant heating rate of 10 °C/min in an inert nitrogen atmosphere.

3. Results and discussion

3.1. Optical properties

The refractive index of optical acrylic PSAs can be controlled by means of a UV-curing process [8,9]. Fig. 1 shows the refractive indexes of acrylic PSAs with different HCA contents. The refractive index of the acrylic PSAs increased with an increase in HCA content in the visible range. In particular, the refractive index with a HCA content of 2.0 phr was much higher than that with a HCA content of 1.0 phr. This illustrates the effect of the HCA content, which increased the refractive index of the polymer, due to the presence of a tetra-functional acrylate, forming a dendrimeric crosslinked polymer network by UV-curing. Generally, the refractive index of a polymer containing a high refractive index functional group is higher than that of a monomer. In this manner, acrylic PSAs with HCA content exceeding 2.0 phr had very high refractive indices that exceeded 1.60 in the visible range. Fig. 2 shows the transmittance of each acrylic PSA sample as measured by UV–visible spectroscopy. The samples should show high transmittance (> 95%), in order to be used in optical films [3]. As shown in Fig. 2, the transmittance of the acrylic PSAs with an HCA content that exceeds 2.0 phr was greater than 95%, demonstrating high transparency in the visible wavelength due to its highly crosslinked structure.

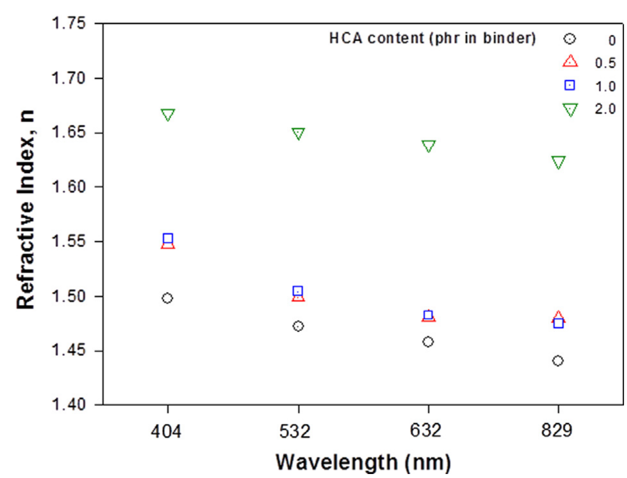

Fig. 1. The refractive indexes of the acrylic PSAs were increased by increasing the HCA content in the acrylic PSA in the visible range.

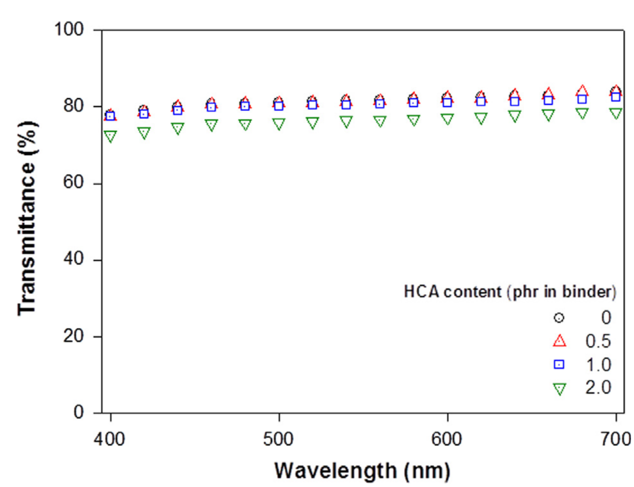

Fig. 2. The transmittance of the acrylic PSAs with a HCA content exceeding 2.0 phr was greater than 95%, demonstrating high transparency in the visible wavelength due to a highly crosslinked structure.

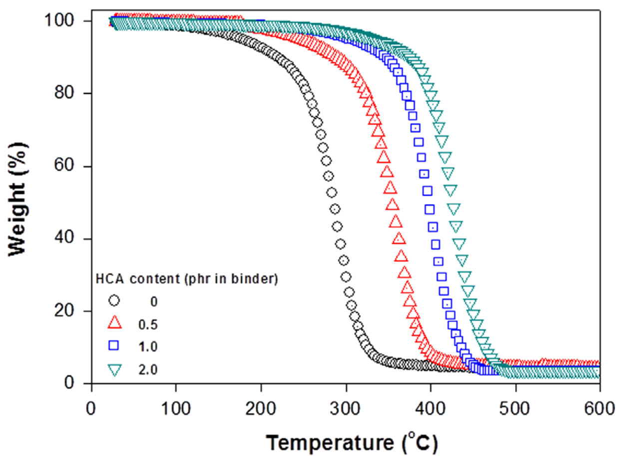

Fig. 3. The thermal stability of the acrylic PSAs was improved with an increase in the HCA content in the acrylic PSAs due to the higher crosslinked structure created by UV-curing.

3.2. Thermal stability

Fig. 3 indicates the thermal stability of UV-cured adhesives at temperatures ranging from 25 °C to 600 °C. The majority of decomposition takes place above a certain temperature, corresponding to the advanced fragmentation of the macromolecules formed during the dehydrogenation reactions, the thermal cracking, and the disproportionation and gasification processes [10]. Major differences were noted as the HCA content. This result suggests that the thermal stability is dependent on the HCA contents due to the higher density of the UV-cured crosslinked networks.

4. Conclusion

In summary, acrylic PSAs were prepared by adding a high refractive index monomer, HCA to improve the optical properties for use in LCDs. Also, UV-curing was investigated for its ability to enhance the thermal stability due to a higher crosslinked structure. As mentioned above, the refractive index and transmittance were increased with an increase in the HCA content. The thermal stability was also clearly improved by increasing the HCA content. Optically clear acrylic PSAs films with HCA have the potential to be used as optical thin adhesive films. Alternatively, the solutions can be used to fabricate multifunctional devices or optical materials. Future studies are essential to improve the performance of acrylic PSAs with HCA so as to increase their adhesion strength further and decrease unreacted monomers during the UV-curing step, thus making them more suitable for applications in various fields.

References

[1] Benedek I, Feldstein MM. Handbook of pressure-sensitive adhesives and products. USA: CRC Press; 2009.
[2] Auchter G, Aydin O, Zettl A, Satas D. In: Satas D, editor. Handbook of pressure sensitive adhesive technology. Warwick, RI: Satas Associates; 1999. p. 444–514.
[3] Chau JLH, Lin Y-M, Li A-K, Su W-F, Chang K-S, Hsu L-C, et al. Transparent high refractive index nanocomposites thin films. Mater Lett 2007;61:2908–10.
[4] Czech Z. Crosslinking of pressure sensitive adhesive based on water-borne acrylate. Polym Int 2003;52(3):347–57.
[5] Joo H-S, Park Y-J, Do H-S, Kim H-J, Song S-Y, Choi K-Y. The curing performance of UV-curable semi-interpenetrating polymer network structured acrylic pressure-sensitive adhesives. J Adhes Sci Technol 2007;21(7):575–88.
[6] Do H-S, Park J-H, Kim H-J. UV-curing behavior and adhesion performance of polymeric photoinitiators blended with hydrogenated rosin epoxy methacrylate for UV-crosslinkable acrylic pressure sensitive adhesives. Eur Polym J 2008;44(11):3871–82.
[7] Joo H-S, Do H-S, Park Y-J, Kim H-J. Adhesion performance of UV-cured semi-IPN structure acrylic pressure sensitive adhesives. J Adhes Sci Technol 2006;20(14):1573–94.
[8] Lee S-W, Park J-W, Kwon Y-E, Kim S, Kim H-J, Kim E-A, et al. Optical properties and UV-curing behaviors of optically clear semi-interpenetrated structured acrylic pressure sensitive adhesives. Int J Adhes Adhes 2012;38:5–10.
[9] Lee S-W, Park J-W, Park C-H, Kwon Y-E, Kim H-J, Kim E-A, et al. Optical properties and UV-curing behaviors of optically clear PSAs-TiO_2 nano-composites. Int J Adhes Adhes 2013;44:200–8.
[10] Yin T, Rong MZ, Zhang MQ, Yang GC. Self-healing epoxy composites—preparation and effect of the healant consisting of microencapsulated epoxy and latent curing agent. Compos Sci Technol 2007;67(2):201–12.