Synthesis and Characterization of Optically Clear Pressure-Sensitive Adhesive

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We synthesized Optically Clear Adhesive (OCA) polymers by free radical polymerizations and cured them as an interlayer between two polyethylene terephthalate (PET) release films. Some fundamental characteristics of OCA polymers including glass-transition temperature (T_g), molecular weight, viscosity, probe tack and peel strength were investigated with the change of methyl methacrylate (MMA) and 2-hydroxyethyl acrylate (HEA) monomers. The optical characteristics of OCA films were also investigated on the change of ripening temperature, high-temperature aging and heat-moisture aging. The resistance change rates of ITO-coated films were measured with heat-moisture treatment for two weeks. The results suggested that the OCA films can effectively protect ITO films and the synthesized OCA polymer can be expected to be applied to touch panel devices. [doi:10.2320/matertrans.M2014425]

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1. Introduction

Touch panels are being used in a wide variety of applications to improve human-computer interaction.^{1–3)} As this technology advances, people have been able to operate computers without mice and keyboard. Because of its convenience, touch screen technology solutions have been applied increasingly to industries, products and services.

Currently, the most widely used is the capacitive touch screen,^{4,5)} which is used in mobile phones, personal digital assistant (PDA), computer numerical control (CNC) panel, etc. As the human body is a conductor, touching the surface of the screen causes a coupling capacitor, and monitoring the change of capacitance can determine the position of the contact.⁶⁾ The advantage is that the transmittance of capacitive touch screen reaches more than 90%. The basic components of capacitive touch screen consist of polarizer, color filter, Indium Tin Oxide (ITO) film^{7,8)} and Optically Clear Adhesive (OCA), etc.

Optically clear pressure-sensitive adhesives are used to adhere optical films to optical elements, such as glass elements or polymeric elements.^{9,10)} The peel adhesion of the OCA on optical films and optical elements must be maintain under conditions of high heat and humidity, otherwise, the delamination of the optical film and/or the optical element from the OCA may lead to undesirable changes in the optical characteristics.^{11,12)} An OCA polymer is formed by polymerizing several (C_1 – C_8) alkyl (meth)acrylate monomers and hydroxyalkyl (meth)acrylate monomers. Their popularity is mainly attributable to optical clarity, weather ability, oxidative and ultraviolet resistance, low toxicity and low cost.

In this study, OCA polymers were synthesized and cured as an interlayer between two polyethylene terephthalate (PET) release films. The OCA films were used in the fabrication of touch panel devices. Some fundamental characteristics of the OCA polymers including glass-transition temperature (T_g), molecular weight, viscosity, probe tack and peel strength were investigated. In a further study, the OCA films with satisfactory weather resistance,

excellent optical transparency and non-corrosive were applied to the assembly of a touch panel, especially, the assembly of ITO film in touch module.

2. Experimental Procedure

2.1 Materials and Purification

2-ethylhexyl acrylate (2-EHA, Aldrich Chemical Co.), butyl acrylate (BA, Kelong Chemical Reagent Co.), methyl methacrylate (MMA, Aldrich Chemical Co.), 2-hydroxyethyl acrylate (HEA, Aldrich Chemical Co.), glycidyl methacrylate (GMA, Chengdu XiYa Chemical Technology Co., Ltd.), benzoyl peroxide (BPO, Kelong Chemical Reagent Co.), tripropylene glycol diacrylate (TPGDA, J&K Scientific Ltd.), FINETACK HARDENER Exp. DN (DN, DIC (Shanghai) Co. Ltd.) was an isocyanate curing agent. Ethyl acetate (EAc, Kelong Chemical Reagent Co.) and methyl ethyl ketone (MEK, Kelong Chemical Reagent Co.) were purified by distillation under reduced pressure.

2.2 Process

2.2.1 Synthesis of optically clear adhesive (OCA) polymers

The polymers of OCA were synthesized using 2-EHA, BA, MMA, HEA, GMA and TPGDA through solution polymerization initiated by BPO in ethyl acetate. Table 1 shows the composition of polymerization. The polymerization was performed in a four-necked flask equipped with a mechanical stirrer, a reflux condenser, a centigrade thermometer and a constant-voltage dropping funnel. The typical synthetic method was as follows. The flask was charged with one-fifth of monomer mixture, 15 mL EAc and 1.0 g BPO, then polymerization was started at 80°C for about 30 min. After polymerization, the remaining monomer, initiator and solvent mixture was dropped into the flask slowly, and the flask was kept at 80°C for 5 h.

We used constant-voltage dropping funnel in order to increase reproducibility and control exactly molecular weight and viscosity. We monitored both temperature and viscosity change of the reaction system, to ensure that the exothermic reaction could be carried out smoothly, and to maintain a low viscosity of the product.

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Table 1 Polymerization formula of OCA polymers.

Components	Samples (g)				
	OCA-1	OCA-2	OCA-3	OCA-4	OCA-5
2-EHA	32.0	24.0	16.0	32.0	32.0
BA	32.0	32.0	32.0	32.0	32.0
HEA	10.0	10.0	10.0	12.5	15.0
MMA	0.0	8.0	16.0	0.0	0.0
GMA	5.0	5.0	5.0	2.5	0.0
TPGDA	1.0	1.0	1.0	1.0	1.0
BPO	0.3	0.3	0.3	0.3	0.3
EAc	80.0	80.0	80.0	80.0	80.0

Fig. 1 Schematic of the preparation of an OCA multilayer film.

2.2.2 Preparation of OCA films

Firstly, the curing agent DN with an amount of 0.3–0.6% was added into the synthesized OCA polymer at room temperature. Secondly, the OCA glue was coated onto the PET release film to a dry thickness of 50 micrometers using wet coating, then dried and cured at 80°C for 3 min. Thirdly, the second PET release film was covered on other side of the OCA film, to obtain a multilayer film with PET/OCA/PET structure as shown in Fig. 1. Finally, the multilayer film was ripened at 50°C for three days to ensure curing reaction completely, and the OCA film product was obtained successfully.

The ITO-coated films were prepared at a constant temperature and humidity (23°C, and 50% RH) environment. The OCA films were covered on the ITO films after removing the PET release film on one side of OCA multilayer film. Then, the samples were dwelled overnight and visually inspected for delamination or bubbling.

2.3 Measurements

Fourier transform infrared spectra (FT-IR) were obtained with a PerkinElmer Spectrum Two spectrometer from 4000 to 500 cm^{-1} on KBr pellets. Differential Scanning Calorimetry (DSC) was performed with a NETZSCH DSC200F3 instrument from -80 to 200°C at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere. An NXS-IIA rotational viscometer was employed to measure the viscosity of OCA at

Fig. 2 FT-IR spectrum of OCA-1 polymer.

different shear rates at $25 \pm 0.2^\circ\text{C}$ after the solid content of each sample was adjusted to be equal by adding EAc or MEK. Gel permeation chromatography (GPC) with an Agilent HPLC-1100 instrument was employed to measure the molecular weights and molecular weight distributions of OCA, while THF was used as the eluent at a flow rate of 1.0 ml/min at 35°C . The probe tack and peel strength of OCA polymers were measured on a PT-6080 tensile tester with a 5 kg load cell, and according to China national standards GB/T 2792-1998. Ultraviolet-visible (UV-Vis) spectra of OCA films were recorded on a UV-visible spectrometer (UV1902PC) from 400 to 700 nm. The optical properties of the OCA films were detected by Transmittance Haze Meter (WGT-S).

3. Results and Discussion

The formation of OCA-1 was confirmed by IR spectroscopy as shown in Fig. 2. The absorption peaks at 2961.8–2876.1 cm^{-1} were assigned to CH_2 and CH_3 , respectively; the absorption peak at 1460.2 cm^{-1} belonged to CH_2 deformation; the strong absorption peak at 1736.0 cm^{-1} was ascribed to ester $\text{C}=\text{O}$ stretching, and 3526.6 cm^{-1} attributed to OH stretching.

The molecular weight data of OCA resins are shown in Table 2. The molecular weight decreased with the increase of MMA content, and the OCA resins increased HEA content show higher molecular weight. Obviously, the polydispersity index (PDI) of OCA resins were about 1.2–1.4, and the polydispersity index increased with the increase of MMA and GMA content; this may be because of various reactivity ratio of acrylic esters and methacrylic esters.^{10,13)}

Examination of DSC data presented in Table 2 show the increase in glass transition temperature as MMA or HEA content increases.

The viscosity of the OCA resin is an important factor that affects wetting and coating properties of substrate.¹⁴⁾ The viscosity of OCA resin was about 281–743 mpa·s at 25°C with 30% solid content. Additionally, the viscosity increased as MMA and HEA content increased. This result is due to the high T_g of PMMA and the hydrogen bond of HEA. Figures 3 and 4 show the relationship of the viscosity of OCA-1 between the solid content, temperature and solvent system.

Table 2 Performance parameters of OCA polymers.

Samples	Mn	Mw	PDI	T_g (°C)	Viscosity (mpa·s)
OCA-1	65200	84800	1.3	-42.5	281
OCA-2	58900	82500	1.4	-33.7	526
OCA-3	56800	79500	1.4	-19.3	743
OCA-4	69600	90500	1.3	-43.1	498
OCA-5	76400	91700	1.2	-43.8	652

Fig. 3 Viscosity of OCA-1 polymer with temperature and solvent system for a solid content 30%.

Fig. 4 Viscosity of OCA-1 polymer with solid content and solvent system for a temperature of 25°C.

Figure 5 shows the probe tack and peel strength of OCA polymers decreased for decrease of flexibility and softness as MMA content increase. Figure 6 shows the peel strength of OCA polymers increased for enhance of hydrogen bond between polymer and matrix as HEA content increased. Conversely, the probe tack of OCA polymers decreased as HEA content increase. This reason might be because the hydrogen bond between the polymer chains reduce the flexibility of the OCA polymer.

The characteristic of the OCA film affects the durability of the touch panel.^{11,12)} The effects of ripening temperature on the transmittance, and aging on the optical characteristics of the OCA film were investigated. The transmittance of OCA-1 films, as a function of ripening temperature, is plotted in Fig. 7. Obviously, the transmittance of OCA films was

Fig. 5 Probe tack and peel strength of OCA polymers as a function of MMA content.

Fig. 6 Probe tack and peel strength of OCA polymers as a function of HEA content.

Fig. 7 Changes in transmittance of OCA-1 film after aging at various temperatures.

increased as the ripening temperature was increased. The optimal ripening temperature was 50 °C, and the transmittance in the visible region reached more than 95%.

Table 3 shows the optical parameters of OCA films after high-temperature or heat-moisture aging. The OCA multi-layer film samples were placed into an 80 °C environment and aged 21 days or placed into an 85 °C/85% relative humidity environment and aged 21 days. These samples were taken out

Table 3 Optical characteristics of OCA films.

	Initial State			Aging Conditions					
				80°C, 21 days			85°C/85% RH, 21 days		
	T_t (%)	H (%)	b^*	T_t (%)	H (%)	b^*	T_t (%)	H (%)	b^*
OCA-1	92.7	0.63	0.71	92.7	0.77	1.13	92.6	0.98	0.85
OCA-2	92.9	0.68	0.74	92.9	0.75	1.05	92.8	1.03	0.81
OCA-3	92.9	0.66	0.67	92.8	0.74	0.97	92.8	1.00	0.75
OCA-4	92.8	0.52	0.58	92.7	0.69	0.78	92.7	0.88	0.66
OCA-5	92.8	0.47	0.41	92.8	0.62	0.69	92.6	0.94	0.60

T_t : Total luminous transmittance, H : Haze, b^* : yellowness

Fig. 8 Resistance change rates of ITO coated films after heat-moisture treatment at 85°C/85% RH.

and dwelled 24 hours in a constant temperature and humidity (23°C, and 50% RH) room before testing. The total luminous transmittances of OCA films without PET release films were nearly unchanged. However, the high-temperature aging caused yellowness increases; the heat-moisture aging caused haze increases. Overall, the extent of these adverse changes was relatively small, and acceptable. These results show that the OCA films possessed a good weather resistance and excellent optical characteristics.

Figure 8 shows the effect of heat-moisture treatment on the resistance of ITO-coated films. The ITO-coated film samples placed into an 85°C/85% relative humidity environment. The samples were taken out and placed into a constant temperature and humidity (23°C, and 50% RH) room for one hour before testing. The resistance change rate of ITO-coated OCA-1 film was only 3.2% after two weeks, about one tenth of the resistance change rate of pure ITO film. The data of resistance change rates of ITO-coated films are shown in Table 4. In addition, there were no obvious acid-base

Table 4 Datasheet of resistance change rates.

	ITO + OCA-1	ITO + OCA-2	ITO + OCA-3	ITO + OCA-4	ITO + OCA-5	ITO-film only
1 day	0.1	0.1	0.2	0.2	0.3	5.5
4 days	1.4	1.2	1.3	1.5	1.6	13.2
7 days	2.6	2.5	2.7	2.6	2.8	18.8
10 days	3.5	3.3	3.5	3.1	3.6	25.1
14 days	3.2	3.4	3.5	3.5	3.8	31.2

components in the formulation of OCA. Accordingly, the OCA film can effectively protect the ITO film, to avoid oxidation and corrosion, improve durability and stability.

4. Conclusion

Optically clear adhesive (OCA) polymers were prepared by free radical polymerizations. The OCA polymers T_g increased as MMA or HEA monomers were incorporated in the polymers. This result may be explained by the hindered rotation due to the presence of methyl substituent in MMA and hydrogen bonding interaction in HEA. For the same reasons, the probe tack of OCA polymers decreased for decrease of flexibility and softness as MMA or HEA increase. The peel strength of OCA polymers increased for hydrogen bonding as HEA increase. The OCA films possessed excellent transmittance in the visible region. The optical characteristics of OCA films almost did not change after high-temperature and heat-moisture aging. The resistance change rate substantially decreased for ITO coated OCA films after heat-moisture treatment. These results suggest that the synthesized OCA polymer can be expected to be applied to touch panel devices.

REFERENCES

- 1) S. J. V. Nichols: *Computer*. **40** (2007) 12–15.
- 2) J. W. Stetson: *Inf. Disp.* **22** (2006) 26–30.
- 3) J. Lee and H. G. Kim: *SID Symp. Digest*. **38** (2007) 1101–1104.
- 4) T. H. Hwang, W. H. Cui, I. S. Yang and O. K. Kwon: *IEEE. T. Consum. Electr.* **56** (2010) 1115–1122.
- 5) M. R. Bhalla and A. V. Bhalla: *Int. J. Comput. Appl.* **6** (2010) 12–18.
- 6) G. Barrett and R. Omote: *Inf. Disp.* **3** (2010) 16–21.
- 7) H. Cho and Y. H. Yun: *Ceram. Int.* **37** (2011) 615–619.
- 8) E. J. Guo, H. Guo, H. Lu, K. Jin, M. He and G. Yang: *Appl. Phys. Lett.* **98** (2011) 011905.
- 9) E. P. Chang and D. Holguin: *J. Adhes.* **81** (2005) 495–508.
- 10) S. J. Lee and L. S. Park: *J. Appl. Sci.* **10** (2010) 1104–1109.
- 11) S. W. Lee and H. J. Kim: *Int. J. Adhes. Adhes.* **50** (2014) 93–95.
- 12) S. W. Lee and H. S. Woo: *Int. J. Adhes. Adhes.* **47** (2013) 21–25.
- 13) Y. C. Leong and N. Gan: *J. Appl. Polym. Sci.* **88** (2003) 2118–2123.
- 14) L. Blankenburg, K. Schultheis, H. Schache, S. Sensfuss and M. Schrödner: *Sol. Energ. Mat. Sol. C* **93** (2009) 476–483.