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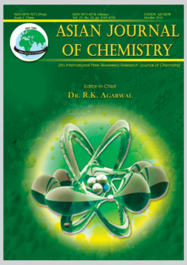

Study on Curing Process and Properties of UV Curable Polyurethane Acrylate Adhesive

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We synthesize a novel UV curable polyurethane acrylate adhesive which can be used in the application of liquid crystal display panel and organic light emitting diode panel. Fourier transform infrared spectroscopy is used to investigate the effects of the curing time, photoinitiator types and their contents,reactive diluent types on the curing behaviour. The electrical and mechanical properties and the water resistivity of the UV-curable adhesive are investigated in this study.

Key Words: FTIR, Polyurethane arylate, UV curing, Water absorption.

INTRODUCTION

Ultraviolet curable adhesives consumes little energy and is environmentally friendly. It has gained increasing attention due to its advantages such as long storage lifetime, solutionless, no volatile gas emission before and after curing, short curing duration, strong adhesion and energy efficient production and has been widely used in areas such as Printed Circuit Board production, plastic adhesion, liquid crystal display installation, electronic components integration and many other fields.

With the rapid development of information technology, there is an increasing demand of display devices and the advanced UV curable adhesive has been used extensively in the production of liquid crystal display and organic light emitting diode. As the main constituent of liquid crystal display is transparent glass, UV curable adhesive is needed in the fabrication process of liquid crystal display to adhere, fix and seal its components, therefore the performance of UV curable adhesive is a key factor affecting the quality of liquid crystal display. The research on how to produce advanced UV curable adhesive that is low cost, reliable, has fast reaction rate in curing, becomes hard after curing with high tensile strength and good shrinkage, high gloss, high solvent resistance and highly electrical insulating is now a hot topic. Wang and Chen[1] have reported how different factors affect the process of polymerization and hence concluded the good condition required to synthesize polyurethane acrylate oligomers, but details about its characteristic is not reported. Zheng[2] added reactive diluents, photoinitiator etc to synthesized polyurethane acrylate oligomers to produce UV curable adhesive and the quantity is determined by analyzing how the quality of liquid crystal display panel fill sealing and metal support fixation is affected under different composition. Zhang *et al.*[3] discussed the technical requirement and application of UV curable adhesive in the liquid crystal display fabrication process. Yao *et al.*[4] used FTIR to track the epoxy acrylate resin system curing process and studied the relationship between radiation time and double bond conversion rate in that system. Hong *et al.*[5] studied how UV light intensity and temperature affects the curing process in epoxy acrylate resin system. Morii *et al.*[6] researched the effect of tensile strength, shrinkage of UV curable adhesive in sealing on liquid crystal display panel. Zhao *et al.*[7] studied the monomers and oligomers types affects the shrinkage and the adhesion strength. Kim and Seo[8] reported the relationship between curing duration and tensile strength. But a systematic study of curing time, type and quantity of photoinitiator and reactive diluents in using FTIR, as well as the water resistance of the UV curable adhesive is still lacking. In this paper we report the curing process of the UV curable polyurethane acrylate adhesive with high curing rate and its some properties.

EXPERIMENTAL

Polyethylene glycol adipate (PEA M = 2000, Shanghai Youcu Company Pte Ltd.), Toluene-2.4-diisocyanate (TDI, Chengdu Kelong Chemical Reagent Company, China), Isobornyl Acrylate (IBOA, Tianjin Tianjiao Material Co. Ltd., China), 2-Hydroxyethyl methacrylate (HPMA,Beijing Eastern Chemical Works,China), Dibutyltin dilaurate (DBTDL, Chengdu Kelong Chemical Reagent Company, China), 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (TPO, Nanjing Chunghosung Technology Co. Ltd., China), 1-hydroxycyclohexyl phenyl ketone (184, *N*Nanjing Chunghosung

Technology Co. Ltd., China), 2-hydroxy-2-methyl-1-phenylpropan-1-one (1173), Benzophenone (BP, Chengdu Kelong Chemical Reagent Company, China).

Synthesis of oligomer: Calculated amount of toluene-2,4-diisocyanate, isobornyl acrylate and dibutyltin dilaurate is added to a four-necked flask that is equipped with a stirrer, a condenser and an addition funnel. Polyethylene glycol adipate is dropped into the reactor slowly while the mixture is stirred and the reaction temperature is controlled between 40 to 60 ºC. After reacting for 4 to 5 h, 2-hydroxyethyl methacrylate is added and reaction continues for another 1 to 2 h at 60 to 80 ºC. Then temperature of above reaction is raised to 70 to 90 ºC and kept for 0.5 to 2 h. In the end mixture is cooled and collected.

UV curable adhesive preparation and curing process: The collected oligomers is mixed with photoinitiator according a required ratio, stirred well and coated (thickness = 0.2 mm) on a glass plate. It was cured in the UV-curing apparatus with a high-pressure mercury lamp (1000 w). The distance between light source and glass plate is 30 cm.

Testing and equipment

GPC testing: Two chromatographic columns of 5 µm by 1 um and 5 µm by 0.01 µm are connected in series with Agilent (US) 1100 HPLC. THF is used as solvent, flow rate is 1 mL per minute and measurement is done at 35 ºC.

Fourier transform infrared spectra: FI-RT670 fourier infrared spectrometer is used to analyze the infrared spectrum. Sample is applied to glass and cured by UV light at room temperature. The C=O bond is unaffected in the curing process and the stretching vibration of the C=C absorption peak at 1600 cm^{-1} is the sum of oligomer and reactive diluents', with the curing process, the chemical structure of C=C bond the changes and so does the IR spectra. So used the C=O bond absorption peak at about 1730 cm^{-1} as the internal standard and monitoring the C=C double bond conversion rate at 1600 cm^{-1} in the curing process to measure the extent of curing in the system.

Contact angle testing: DSA100 light contact angle measurement unit from KRUSS, Germany is used to measure the contact angle. Five measurements are taken from each sample and their average is taken.

Water absorption testing: Mass is measured by electronic balance under dry condition and is recorded as M_0. After soaked in distilled water for certain period, the mass is measured as M_1. Then the mass ratio between soaked mass and dry mass is calculated by the formula below:

$$W = (M_1 - M_0)/M_0 \times 100\ \%$$

where, W is the water absorption, M_0 is the dry mass and M_1 is the mass after the sample is soaked in water.

Mechanical property testing

80º peel strength test: The UV curable adhesive is applied evenly on a glass plate and the thickness is controlled at 0.2 mm. After curing, it is cut into strips of 200 mm length and 20 mm width. The 180º peel strength test is performed according to XLW electronic tensile testing machine from Jinan Languang.

Tensile stretch test: The UV curable adhesive is cured and cutted into a dumbbell shape of 100 mm length, 20 mm width and 3 mm thickness. XLW electronic tensile testing machine from Jinan Languang is used to measure the tensile stretch.

Electrical resistance testing: ZC43 ultra high resistance meter from Shanghai Diliu Dianbiao Factory is used. Three measurements are taken from each sample and the average is taken.

RESULTS AND DISCUSSION

Curing process study

Relationship between curing time and conversion: FTIR is used to track the relationship between exposure time of polyurethane acrylate under UV light and the double bond conversion rate. Results are shown in Figs. 1 and 2 below.

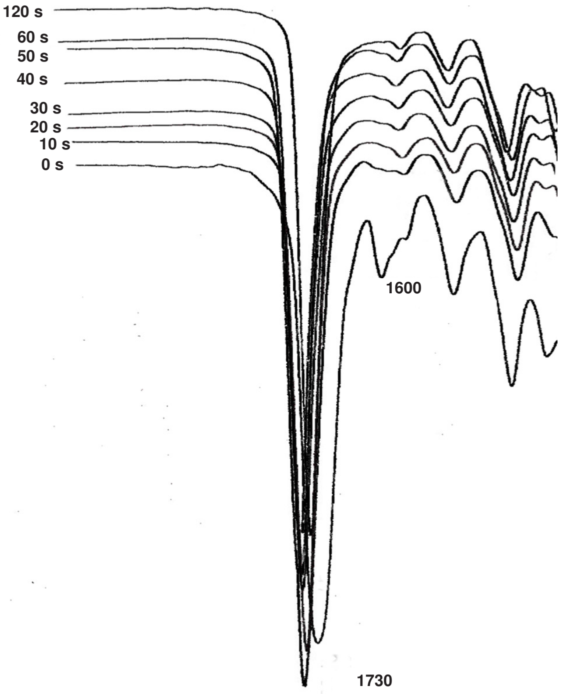

Fig. 1. Part of FTIR spectra of different curing times

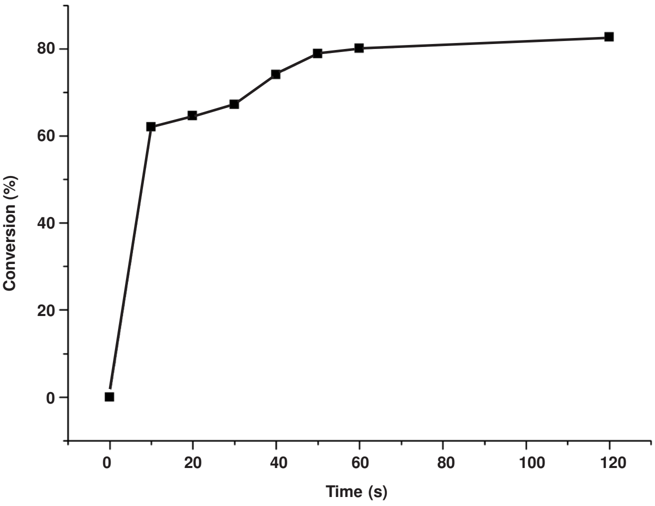

Fig. 2. Curing time against conversion

It is observed in Table-1 that double bond conversion has reached 62 % after exposing under the UV light for 10 sec, indicating that the polymer has a high degree of conversion at the beginning. After 40 sec, the double bond conversion shows little change and the conversion increase becomes gradual. Until the curing time to 60 sec the double bond conversion rates and no significant increase. This is because the viscosity of system increasing as the reaction is carried out and the reactive of the active free radicals decreases as the segment increases and it has less changes interacting with the remaining double bonds. The free volume for molecular movement as well as the room for monomers movement decreases, resulting in decreased conversion increase and 100 % conversion cannot be achieved. In short, UV adhesive has a fast curing at the beginning and decreases thereafter. The optimal curing time is about 40 sec.

TABLE-1
RELATIONSHIP BETWEEN CURING TIMES AND DOUBLE BOND CONVERSION

Curing time (sec)	1600 cm^{-1} Integrated peak area	1730 cm^{-1} Integrated peak area	Area ratio (1600 cm^{-1} /1730cm^{-1})	Double bond conversion (%)
0	1.622	20.131	0.0806	0.0
10	0.085	2.768	0.0307	62.0
20	0.079	2.765	0.0286	64.6
30	0.074	2.808	0.0264	67.2
40	0.057	2.731	0.0209	74.1
50	0.048	2.821	0.0170	78.9
60	0.045	2.789	0.0160	80.1
120	0.035	2.454	0.0140	82.7

Relationship between variety of initiator and conversion: Photoinitiator is an important component in the photo-cruing system, it affects whether the oligomer and reactive diluents in the system can change from liquid state to solid state quickly. Depending on the initiating principle, photoinitiator can be classified into free radical photoinitiator and cationic photoinitiator and the former is generally used. Based on different mechanism of free radical, the free radical photoinitiator can further be classified into the photolysis type and the hydrogen capture type. Under UV light, hydrogen capture photoinitiator forms a compound intermediate state through charge transfer and generate active free radicals by the proton transfer. Photolysis photoinitiator initiates free radical from the absorption of UV light by the radical of α-decompose reaction, which groups is easy to occur in the molecular structure. Benzophenone is hydrogen capture type, while 1-hydroxycyclohexyl phenyl ketone (184), 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (TPO) and 2-hydroxy-2-methyl-1-phenyl propane-1-one (1173) is photolysis type. Different photoinitiator has different initiator efficiency and Table-2 shows the double bond conversation of UV adhesive containing different types of photoinitiator, after exposed to UV light for 40 sec. It is observed that hydrogen capture of benzophenone showed virtually no reaction after 40 sec exposure. This is because in that system, benzophenone must work with compounds containing active hydrogen to start the reaction. There is no effect when benzophenone is used alone.

In general, using multiple photoinitiator can greatly enhance the double bond conversation. As shown in Table-2, the curing speed when 2,4,6-trimethylbenzoyldiphenyl phosphine oxide and 1-hydroxycyclohexyl phenyl ketone are used together is much higher than when either one is used alone. The Maximum absorption wavelength of 1-hydroxycyclohexyl phenyl ketone is 333 nm and that of 2,4,6-trimethyl benzoyldiphenylphosphine oxide is 366 nm. Under UV exposure, the two photoinitiator can effectively make use of the UV energy of both waveband of 333 nm and 366 nm from the high pressure mercury lamp, which equals to increase the UV light intensity. By using photoinitiators with different characteristic absorption wavelength together, curing speed can be boosted and the use of expensive photoinitiator can be reduced and hence the cost.

TABLE-2
RELATIONSHIP BETWEEN PHOTOINITIATOR TYPE AND DOUBLE BOND CONVERSION

Photo initiator type	1600 cm^{-1} Integrated peak area	1730 cm^{-1} Integrated peak area	Area ratio (1600 cm^{-1} /1730 cm^{-1})	Double bond conversion (%)
TPO	0.089	2.903	0.0310	61.5
184	0.180	2.653	0.0678	15.9
1173	0.061	2.744	0.0222	72.4
BP	-	-	-	-
184 + 1173	0.095	2.687	0.0350	56.6
184 + BP	0.065	2.864	0.0227	71.8
184 + TPO	0.057	2.731	0.0209	74.1

Relationship between photoinitiator content and conversion: Table-3 shows the double bond conversion under the same photoinitiator for the same curing time, but different dosage. Generally in the photo-cruing system, the double bond conversion increases with the dosage of photoinitiator, yet from experimental results it is found that conversion does not necessary increase with the content of the photoinitiator. In Table -3, high conversion rate is found when the concentration of 184 and 2,4,6-trimethylbenzoyldiphenyl phosphine oxide is 2.4 % (wt), 3.0 % (wt) and 0.8 % (wt), 1.0 % (wt) respectively, while conversion rate becomes low when the photoinitiator concentration is 4.5 % (wt) and 1.5 % (wt). This is because as photoinitiator content increases, concentration of free radicals generated due to photolysis of photoinitiator increases and concentration of radical segment increases rapidly too, monomers consumption rate increases and the viscosity of the system rise rapidly, resulting in gel effect happening earlier and caused the free radicals to be quenched quickly and eventually brought down the conversion. If the photoinitiator content is too low, photoinitiator is soon fully consumed and concentration of free radical segment will drop shortly after the reaction starts, hence causing low conversion. Therefore the optimal concentration of 1-hydroxycyclohexyl phenyl ketone is 2.4 % (wt) to 3.0 % (wt) and that of 2,4,6-trimethylbenzoyldiphenyl phosphine oxide is 0.8 % (wt) to 1.0 % (wt).

Relationship between curing depth and double bond conversion: The same sample is analyzed at different depth using FTIR and the double bond conversion at surface, middle layer and inner layer is shown in Table-4.

TABLE-3
RELATIONSHIP BETWEEN PHOTOINITIATOR CONTENT AND DOUBLE BOND CONVERSION (CURING TIME 30 SEC)

Photoinitiator content	1600 cm^{-1} Integrated peak area	1730 cm^{-1} Integrated peak area	Area ratio (1600 cm^{-1} /1730 cm^{-1})	Double bond conversion (%)
184 1.5 % (wt) TPO 0.5 % (wt)	0.126	2.848	0.0442	45.2
184 2.4 % (wt) TPO 0.8 % (wt)	0.068	2.881	0.0236	70.7
184 3.0 % (wt) TPO 1.0 % (wt)	0.074	2.808	0.0264	67.2
184 4.5 % (wt) TPO 1.5 % (wt)	0.085	2.866	0.0297	63.2

TABLE-4
RELATIONSHIP BETWEEN CURING DEPTH AND DOUBLE BOND CONVERSION (CURING TIME 30 SEC)

	1600 cm^{-1} integrated peak area	1730 cm^{-1} integrated peak area	Area ratio (1600 cm^{-1} /1730 cm^{-1})	Double bond conversion (%)
Inner layer	0.058	2.815	0.0206	74.4
Middle layer	0.059	2.905	0.0203	74.8
Surface	0.074	2.808	0.0264	67.2

It can be observed that the curing at the surface is obviously not as good as that of the middle and inner layer, as shown by the lower double bond conversion. This is possibly due to oxygen inhibition effect. As the sample curing in air, the presence of oxygen consumes free radical and decreases the reaction rate, thus the inner layer curings, but the surface does not and becomes sticky. Oxygen agglomeration can even generate large amount of peroxide that has the structure of such as hydroxyl groups, carbonyl groups and peroxy groups and affect the physical and chemical property and stability of the cured film. In practice covering the sample surface with the transparent membrane can help to isolate oxygen and solve the problem.

Relationship between reactive diluents and conversion: In the photocuring system, reactive diluents can reduce the viscosity of the system and increase the flowability of the adhesive. It contains unsaturated groups and can cause the photocuring reaction and thus increase the polymerization rate of the whole system. As shown in Table-5, as the amount of isobornyl acrylate (IBOA) decrease, curing rate increases. This is possibly because the steric hindrance of isobornyl acrylate is larger than 2-hydroxyethyl methacrylate, thus it is harder to react with oligomers in the curing process, resulting in slower curing speed.

TABLE-5
RELATIONSHIP BETWEEN REACTIVE DILUENTS AND DOUBLE BOND CONVERSION (CURING TIME 40 SEC)

	1600 cm^{-1} Integrated peak area	1730 cm^{-1} Integrated peak area	Area ratio (1600 cm^{-1} /1730 cm^{-1})	Double bond conversion (%)
HPMA (10 %) IBOA (40 %)	0.092	2.460	0.0374	40.8
HPMA (20 %) IBOA (30 %)	0.057	2.731	0.0209	74.1
HPMA (30 %) IBOA (20 %)	0.123	2.642	0.0465	79.4

Cured adhesives properties study:

Molecular mass and distribution study: The molecular mass of oligomers (Fig. 3) and its distribution has obvious impact on the property of the cured adhesive. When the molecular mass of oligomers is small, the density of double bond increases, hence the absolute value of double bond conversion after the curing of UV adhesive is high. Thus the shrinkage is large and because of the shrinkage stress, the sample becomes brittle after curing and hence the tensile strength is relatively low. On the other hand, when the molecular mass of oligomer is high, the soft segment becomes longer and more flexible. Due to the reduction of per unit volume of oligomer and the amount of double bonds, not only the double bond conversion and the shrinkage decreases, but also the cohesive force of polymer, causing the tensile stress and the adhesion to decrease. Besides, system viscosity will increase when the molecular mass of oligomer is too high. The GPC test result of prepolymer (Table-6) shows that when the molecular mass of oligomer is about 13000, the viscosity and tensile strength of such oligomer is relatively good.

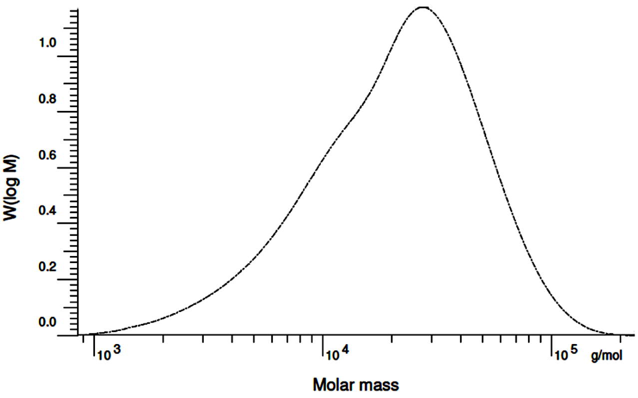

Fig. 3. Molar mass and distribution of oligomer

TABLE-6
MOLAR MASS AND DISTRIBUTION OF OLIGOMER

Sample	Mn	eMw	Mz	My	D
Oligomer	13425	27999	45661	27999	2.0856

Electrical resistance testing: Some circuit of liquid crystal displays are outside the monitor. Since the distance of these wire are very short, slight contaminants such as dirt and moisture can cause electrical disturbance. Hence UV adhesive is required to provide sealing protection and the adhesive must be highly insulating to prevent disturbance or short circuit among the wires. To ensure insulation, there must be very little amount of charged ion in the cured adhesive. Since all constituents of UV curable adhesive are uncharged organic materials, its resistivity should be very high theoretically. The measured surface resistivity is 4.02×10^{13} Ω cm, volume resistance is 4.06×10^{12} Ω, which can meet the requirement as the sealant for liquid crystal display panel.

Mechanical properties: The adhesion of UV curable adhesive is determined by the property of oligomer and reactive diluents. There are a lot of polar groups in oligomer and reactive diluents such as hydroxyl group, ether link, ester link and so on. Since the adhered glass is also polar, so the adhesion is very strong. Meanwhile, the UV curable adhesive should have some flexibility, to prevent it from deforming when adhering. It is found through experiment that the 180 ° peel strength of UV curable adhesive is 22.63 N cm^{-1}, elongation is 218 %. Such property is generally able to meet the application requirement.

Water resistivity study: In prolonged usage of liquid crystal display, its working environment has a significant impact on its durability. Especially in humid environment, the atmospheric moisture may enter UV adhesive and change its properties, such as increasing the electrical conductivity, which may cause short circuit. Therefore, the water resistivity of UV adhesive is a key factor determining its quality. The water resistivity property is mainly determined by the affinity for water and water absorption of the adhesive.

Water contact angle testing: When liquid and solid surface are in touch, smaller contact angle indicates better compatibility and wettability and vice *versa*. Therefore, hydrophilicity can be obtained by comparing the water contact angle. It can be observed when the amount of oligomer is fixed, with the increase in 2-hydroxyethyl methacrylate content and decrease in isobornyl acrylate content, the contact angle with water decreases, showing better hydrophilicity. Therefore, increasing 2-hydroxyethyl methacrylate contact will enhance the hydrophilicity of UV curable adhesives. This is possibly because 2-hydroxyethyl methacrylate contains more hydroxyl group, which can form weak hydrogen bonds with water molecule when the sample is in contact with water, thus causing higher polarity and higher hydrophilicity, which is indicated by smaller contact angle with water.

Water absorption testing: As shown in Fig. 4, when the content of HPMA increases in the system, water absorption changes obviously. After 24 h of soaking, the water absorption is 0.62, 1.00 and 2.18 % when the 2-hydroxyethyl methacrylate content is 10 % (sample A), 20 % (sample B) and 30 % (sample C) respectively (Table-7). Thus 2-hydroxyethyl methacrylate content is a key factor affecting the water absorption. This is possibly because the hydroxyl group in 2-hydroxyethyl methacrylate can easily forms hydrogen bonds with water molecules and hence cause the water absorption to increase. However, with constant amount of oligomer, decrease in 2-hydroxyethyl methacrylate comes with increase in isobornyl acrylate and will eventually cause the adhesive to have bad flexibility and adhesivity after curing. In light of the above argument, the optimal content of 2-hydroxyethyl methacrylate is 20 %.

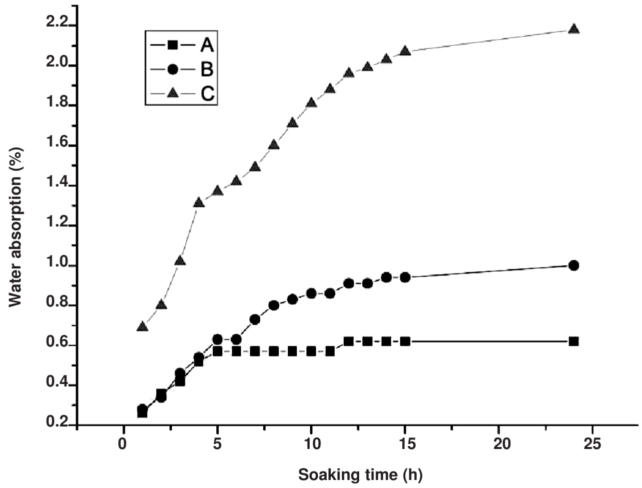

Fig. 4. Water absorption of UV curable adhesive against time

TABLE-7
MEASURED RESULT OF CONTACT ANGLE OF UV ADHESIVE

	A (10 % HPMA)	B (20 % HPMA)	C (30 % HPMA)
Contact angle	74.8°	74.5°	73.1°

Conclusion

It is found through FTIR analysis that curing process happens mainly at the initial stage of UV light exposure, after 40 sec of exposure, the double bond conversion increases slowly.

Using multiple photoinitiator together results in better efficiency than using single photoinitiator. There exists optimal amount dosage of photoinitiator, over the dosage will result in slow curing process. In this system, the optimal content of 184 is 2.4 to 3.0 % and that of 2,4,6-trimethylbenzoyldiphenyl phosphine oxide is 0.8 to 1.0 %.

When sample cures in air, due to oxygen inhibition effect, the inner layer may cured, but the surface did not and becomes sticky.

In this photo-cruing system, curing speed increases with the decrease of reactive diluent isobornyl acrylate. This is possibly due to the larger steric hindrance of isobornyl acrylate, which makes it difficult to react with polymer during curing and slowed the curing speed of the system.

From GPC testing of oligomer, its molecular mass is found to be 13425. Under such condition, the electrical and mechanical properties of the adhesive is able to meet application requirement. For the same type of UV curable adhesive, the hydroxyl group content in the reactive diluent is the key factor determining the water resistivity. After considering the water resistivity and other properties, the optimal concentration of 2-hydroxyethyl methacrylate is found to be 20 %.

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