Research Article

Synthesis and Properties of UV Curable Waterborne Polyurethane Acrylate Based on Modified Castor Oil

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Abstract In this study, castor oil was modified to prepare hydroxyethyl methyl acrylate (HEMA) capped waterborne polyurethane-acrylate (UV-PUA) via *in-situ* and anionic self-emulsifying method. Ultraviolet (UV) curable UV-PUA film was obtained with IRGACURE *819* as photoinitiator. The properties of UV-PUA dispersions, such as appearance, viscosity and average particle size were investigated. The structure and thermal stability of UV-PUA film were characterized by Roman spectroscopy and DTG. Some mechanical properties of UV-PUA films, such as hardness, adhesion ability and water absorption property were measured. It was found that the viscosity of UV-PUA dispersion decreased while the average particle size increased with the increasing of $n_{(NCO)}/n_{(OH)}$ value. The decomposition temperature of the UV-PUA film shifted to higher temperature as increasing of NCO/OH molar ratio. The C=C bond absorption peak at $1640cm^{-1}$ for UV-PUA film disappeared after UV radiation.

Keywords Modified castor oil, waterborne polyurethane acrylate, UV-curing film, property

Introduction

The research on environment friendly coatings with low or no VOC content has been sitimulated by environmental concerns and health related issue since last mid-century [1]. So various type of coating such as high solid [2], water dispersible [3], powder [4], radiation (UV/EB) curing coatings [5-6] have been developed. Among them, the UV-curing technology has been commonly used in various industrial sectors for its advantages of environmental protection, lower energy consumption, high curing speed, rheological controlling, and adaptation to spraying [7-8]. UV-PUA, as one of the important type, has attracted great interest in the coatings and adhesives due to its unique properties, such as outstanding adhesion, excellent flexibility and chemical resistance [9-12].

Further, the use of bio-based feedstock in both academic and industry laboratories has attract more and more interests for the shortage of fossil resource. The bio-based feedstock can be derived from natural and abundantly available. Their use would contribute to global sustainability. The sustainable resources are comparatively easy to handle with no or less toxicity and health related issues. Technical innovations continue to drive renewable resources based materials toward more industrial applications. In this context, many kinds of raw materials from renewable resources such as plant oils, rosins, terpenes, and sugars have been investigated [13-15].

Castor oil as a renewable material is attracting a lot of interest. The oil is obtained from extracting or expressing the seed of a plant. The oil is not only a naturally occurring resource, it is inexpensive and environmentally friendly. Castor oil is a unique naturally-occurring polyhydroxy compound, so it has been as a starting material for many industrial chemical products, such as paints, coatings, inks, lubricants and a wide variety of other products [16-18].

The aim of the present work was to utilize modified castor oil to develop the UV- PUA. The first step was to esterify castor oil by maleic anhydride and get a modified castor oil (MCO) with a hydroxyl value of 112 mg KOH/g and an

acid number of 42 mg KOH/g. Then UV-PUA dispersions were synthesized with MCO, PTMG, IPDI, BD, DMPA and HEMA as raw materials. The effects of $n_{(NCO)}/n_{(OH)}$ on the properties of synthesized UV-PUA dispersions and their cured films were evaluated.

Experimental

Materials

Maleic anhydride modified castor oil(MCO) made according to our previous work [19], Polytetrahydrofuran glycol (PTMG, Mw = 1000, Aladdin) was dried and degassed for 5 h at 80°C, 1~2 mmHg, before use. TEA, acetone and 1,4-butanediol (BD, Fuchen Chemical Reagents Factory, Tianjin, China)，were used after being treated with a molecular sieve. Other first grade reagents, i.e. isophorone diisocyanate (IPDI, Aladdin), 2,2-Dimethylol propionic acid (DMPA ,Aladdin), Hydroxyethyl methyl acrylate (HEMA, aladdin) and N-methyl-2-pyrrolidinone (NMP, Aladdin) and IRGACURE *819* (BASF)were used without further purification. Water was distilled and deionized.

Preparation of UV-PUA dispersion

Polymerization was performed in a 250ml round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, and condenser with drying tube. Reaction was carried out in an N_2 atmosphere in a constant-temperature oil bath. IPDI, MCO and polyol were charged into the reactor, then dibutylbis (lauroyloxy) tin (DBTL) was added as catalyst and the mixture was heated at 60°C until the theoretical NCO value was reached, as determined by the di-n-butylamine titration method. After that, DMPA and BD resolved in NMP were added to the mixture and the reaction proceeded at 70°C until the theoretical NCO value was reached. During the reaction acetone was added properly to decrease the viscosity. Then, the reactant was cooled down to 60°C. HEMA was added to obtain HEMA-capped urethane oligomer at 60°C for 5 h. Oligomer capped by HEMA was cooled to 50°C, and the carboxylic acid groups were neutralized by triethylamine (TEA) during the next 0.5 h. Finally, a calculated amount of the deionized water was dispersed into the system under vigorous stirring at the room temperature. Keeping stirring for 45 min, the UV-PUA dispersion was obtained. The basic recipe is listed in Table I.

Preparation of UV-PUA Coating Film

Mixed the newly synthesized UV-PUA dispersion and IRGACURE *819,* then casted the mixture onto a poly (tetrafluoroethylene) drying, allowing it to dry at room temperature for a week insuring the water fully evaporate before UV-curing. Using ultraviolet curing machine for radiation curing film, with the UV light that was produced by a lamp (main wave length: 365 nm, the power of the lamp: 18 W, and the distance between the sample and the center of UV lamp was 15 cm) , irradiating 30 s, the IRGACURE *819* was activated and the radicals could be produced. The formed radicals broke the acrylate double bond of UV-PUA that resulted in crosslinking, then the UV-PUA film could be obtained.

Characterization

The viscosity of the UV-PUA dispersions were measured by a numerical viscometer (NDJ-9S, Shanghai Precision and Scientific Instrument, Shanghai, China); when the shear rate was 2000 s21, the high shear rate warranted highly reliable measurements at a temperature of 25°C.The average particle size of UV-PUA dispersions were determined by a Mastersizer 2000 particle size analyzer (Malvern Instruments) . The adhesion properties of UV-films was tested according to GB/T 9286-1998(eqv ISO 2409: 1992) The hardness was measured with a sclerometer (KYLX-A, Jiangdu Kaiyuan Test Machine, Jiangdu, China), measurements were done three times for each sample, and the average value was calculated. Raman spectra were recorded with a Thermo Scientific NEXUS 670 spectrophotometer. Thermal gravimetric analysis of film was carried out using a TGA instrument (TA instruments) at a heating rate of 10°C/min over a temperature range of 30°C~600°C. The measurements of water absorption or swelling degree of the UV-PUA coating films were the same procedures as follows. The films were cut into the size of 30 mm ×30 mm and put into water at 25°C after being weighted. After 24 h, the film was taken out, rub dry by

wiping off the surface liquid with a piece of filter paper, and then weighted again. The water absorption (or swelling degree), ω, was calculated by as follows:

$$\omega = \frac{m_2 - m_1}{m_1} \times 100\%$$

where m_1 is the mass of the film before being put into the liquid, m_2 is the mass of the film after being put into the liquid.

Table 1: The Basic Recipe for UV-PUA

Sample	$n_{(IPDI)}/n_{(PTMG+MCO)}$	$n_{(NCO)}/n_{(OH)}$	-COOH%[b,c]	$m_{(PTMG)}:m_{(MCO)}$ [a]
UV-PUA1.2	4.0	1.2	1.5	1:1
UV-PUA1.4	4.0	1.4	1.5	1:1
UV-PUA0-1	4.0	1.4	1.5	0:1
UV-PUA1.6	4.0	1.6	1.5	1:1
UV-PUA1.8	4.0	1.8	1.5	1:1
UV-PUA2.0	4.0	2.0	1.5	1:1

a $m_{(PTMG)}:m_{(MCO)}$: the mass ratio of PTMG and MCO

bThe content of -COOH is 1.5% on the basis of the solid content of the UV-PUA dispersions.

cThe neutralization degree of -COOH in UV-PUAs is 100%.

Results and Discussion

Properties of UV-PUA dispersions

Table 2: The characteristics of UV-PUA dispersions

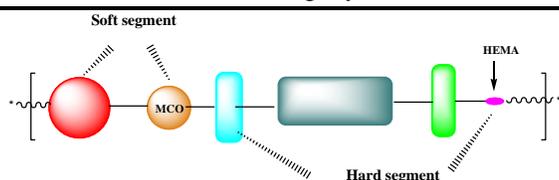| Sample	Appearance	Viscosity (s)	Average particle size (nm)
UV-PUA1.2	transparent, slightly blue	11.97	25.2
UV-PUA1.4	transparent, slightly blue	10.90	34.8
UV-PUA0-1	Milkiness, slightly blue	10.44	137.9
UV-PUA1.6	Semitransparent, slightly blue	10.73	76.4
UV-PUA1.8	Milkiness, slightly blue	10.12	95.3
UV-PUA2.0	Milkiness, slightly blue	9.48	158.7

Figure 1: Composition of UV-PUA

The appearance, viscosity and average particle size of UV-PUA dispersions were listed in Table 2. As can be seen in Table 2, the appearances of UV-PUA1.2 and UV-PUA1.4 dispersions are transparent and slightly blue, but UV-PUA0-1,UV-PUA1.8 and UV-PUA2.0 dispersion are milkiness. In waterborne polyurethane dispersions, the appearance and average particle size are mainly governed by the hydrophilicity of the PU. However, the carboxyl groups in the present system were fixed to a same content, so the appearance and average particle diameters were mainly affected by n(NCO)/n(OH) and m(PTMG):m(MCO). As the results shown, the hydrophilicity decreases with the increasing of n(NCO)/n(OH) , this may be due to the following two reasons. First, as n(NCO)/n(OH) increases, NCO groups remaining in the reaction mixture increases, they react with water during dispersing process, resulting in carbamido components, and sequentially the polymer chain's flexibility decreases. UV-PUA with flexible chains will deformed more easily and dispersed into smaller particles in water. Second, the carbamido groups are strong polar and they would distribute in the surface of the particles and cause reaction heat increase, which can heighten the viscosity of the particles and make them easy to stick together and hard to disperse under shear force, resulting in bigger particles [20]. UV-PUAs had three kinds of structures of hard segment supplied from IPDI, DMPA and

HEMA monomers and soft segment provided from polyether polyol and MCO as shown in Fig. 1 . The viscosity of an oligomer is usually related to the segment density within the volume of a molecule, intermolecular chain entanglements, and inter/ intramolecular hydrogen bonds formed [21]. The viscosity of UV-PUA curable system is considered as one of the most important parameters, affecting the work ability and the photopolymerization rate of the cured film. As can be seen in Table 1, the apparent viscosity of UV-PUA dispersion decreased with the increase of $n_{(NCO)}/n_{(OH)}$, because the decrease of the chain extender content could lead to lower molecular weight and less branched chains on the backbone chains, which would result in lower viscosity. As for UV-PUA0-1, the viscosity was smaller and the average particle size is bigger than UV-PUA1.4, this is mainly due to more MCO was introduced into the polymer. The irregular long branch structure of MCO inhibited the formation of ordered structure of hard segments, which resulted in the increase of hydrogen bond inter-molecular and cause to form bigger particles.

Structure characterization of the UV-PUA film

Raman spectroscopy is most sensitive to highly symmetric covalent bonds and able to provide a wealth of information about their structure. In order to characterize the C=C groups in the polymer. The structures of the UV-PUA films were characterized by Raman spectra as shown in Fig. 2. The disappearance of the NCO band at 2270 cm^{-1} illustrated that the NCO groups had completely been reacted. Besides, it could be seen that there was a absorption pattern of C=O stretching region at 1720 cm^{-1}, which might be attributed to the presence of acrylate groups. The absorption peak of C=C usually at 1640 cm^{-1} (C=C), but after UV radiation, the C=C bond absorption peak in the spectrum of UV-PUA film disappeared, which illustrated that the C=C bond of the polyurethane chains has been polymerized [22-23].
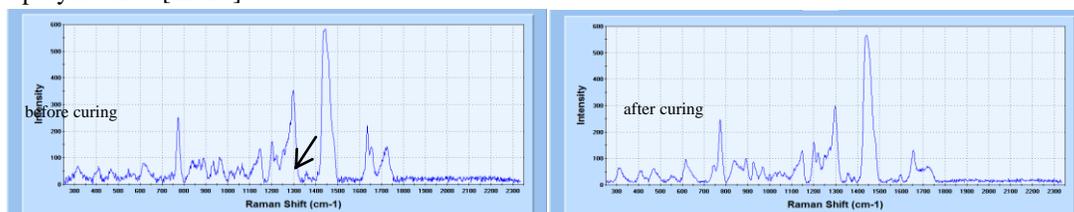

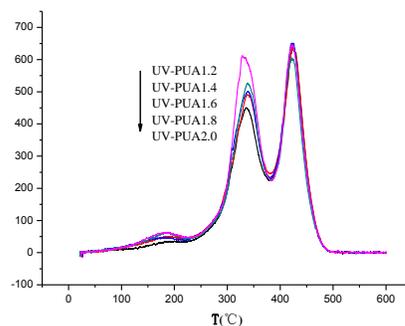*Figure 2: Roman spectrum of UV-PUA film*

TG analysis

Figure 3: DTG traces of UV-PUA films with various NCO/OH molar ratios

Table 3: Decomposition temperatures for UV-PUA films and charge residues

Sample	Degradation 10%	Degradation 50%	Degradation 90%	Charge residue at 500 (%)	T_{MAX1}	T_{MAX2}
UV-PUA2.0	276.89	374.52	440.90	1.62%	337.30	429.33
UV-PUA1.8	261.57	368.06	440.11	1.22%	334.45	427.32
UV-PUA1.6	262.56	364.64	439.36	1.20%	329.45	421.97
UV-PUA0-1	261.33	361.76	436.67	1.08%	343.73	426.41
UV-PUA1.4	249.54	357.81	434.34	0.64%	328.40	420.79
UV-PUA1.2	25216	356.84	439.07	0.47%	328.46	421.87

DTG traces of UV-PUA films with various NCO/OH molar ratio were presented in Figure3. The figures indicate that a weight loss less than 5% occurs at about 150~200ºC, as a result of releasing trapped solvent and decomposing of some peroxide linkages produced from MCO containing double bond. In the first stage of degradation, a rapid weight loss started at approximately 250ºC and continued up to 340~360ºC. It is well established that the amount of weight loss of this region was correlated with the hard-segment concentration [24]. As shown in Figure 3, this part of the degradation correlates with IPDI–DMPA–HEMA segment, while the second peak started at 380ºC reflected the degradation of the soft segment (PTMG-MCO segment). The degradation percentages and maximum peak temperatures of the first step, Tmax1, as well as the equivalents of the second step, Tmax2, can qualitatively characterize the degradation of the UV-PUA films. Table 3 summarizes DTG parameters of the UV-PUA films. The results indicate good thermal stability for the UV-PUA films with 10% appreciable weight loss until well above 250°C. The onset temperatures for hard-segment degradation range from 328.46 to 337.30°C, while the equivalents for soft-segment degradation fall in between 421.87 and 429.33°C. All the results showed that the decomposition temperature shifted to higher temperature as increasing of NCO/OH molar ratio. In this investigation, the HEMA content increases with NCO/OH molar ratio increases as more NCO groups were ended with HEMS. This might cause more cross linking among polymer after UV irradiation as shown in figure 4 .
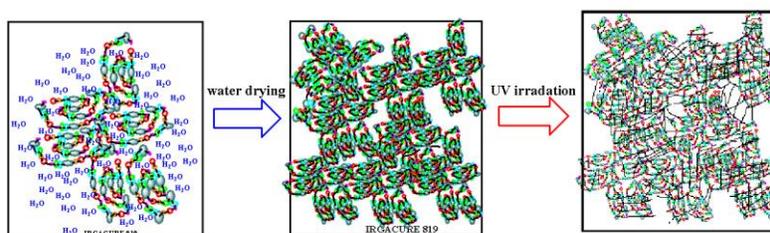

Figure 4: Film forming process of UV-PUA

Physical properties

The physical properties of UV- PUA cured films is shown in Table 4. As more HEMA are incorporated into the UV-PUA backbone, adhesion vary only slightly and kept at 1grade, whereas hardness and water resistance increases substantially. This may be attributed to more interchain interaction among polymer. More MCO will increase the water resistance of the UV-PUA cured film.

Table 4: Physical properties of UV-PUA film

Sample	Adhesion(grade)	Hardness(shore A)	Absorption of water (%)
UV-PUA1.2	1	94.14	20.67
UV-PUA1.4	1	94.78	21.37
UV-PUA0-1	1	90.42	10.00
UV-PUA1.6	1	96.68	22.65
UV-PUA1.8	1	97.30	17.57
UV-PUA2.0	1	98.56	15.26

Conclusions

A series of UV-PUA dispersions and its cured films were prepared in this paper. The effects of n(NCO)/n(OH) on the properties of UV-PUA dispersions and their cured films were studied. It was found that the viscosity of UV-PUA dispersion decreased with the increasing of $n_{(NCO)}/n_{(OH)}$ value. While the average particle size of UV-PUA dispersion increased as $n_{(NCO)}/n_{(OH)}$ increases. The UV-PUA cured films all have good thermal stability and have a first weight loss at approximately 250ºC. The decomposition temperature of the UV-PUA film shifted to higher temperature as increasing of NCO/OH molar ratio.The Raman spectrum showed that the C=C bond absorption peak at 1640cm^{-1} for UV-PUA film disappeared after UV radiation. The hardness and water resistance of the cured films increased as more HEMA incorporated into the UV-PUA.

Acknowledgments

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