Preparation of Water-borne Polyurethane-acrylate (PUA) and Application to UV-curing Coatings on the Package of Paper

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Abstract

In this paper two kinds of UV-curing water-borne resins were prepared from toluene diisocyanate (TDI). The polyurethane-acrylate resins have has been synthesized by the serial steps synthetic method. The content of carboxyl group (-COOH), and molecular weight of Polyethylene Glycol (PEG) and the content of unsaturated double bonds (-CH=CH_2) were optimized by the orthogonal experiment. The reaction conditions were investigated, one-step vs. multi-step synthesis procedure, order of reagent addition, neutralization agent, type of inhibitor and its water-solubility. The resulting resin had excellent performance when the content of carboxyl group (–COOH) was 3.0 $wt\%$, the content of unsaturated double bonds (-CH=CH_2) was 3.0 $wt\%$, and molecular weight of PEG was 600. The influences of initiator content, dry time, dry temperature on UV-curing rate were discussed. The bulk performance of the new resin was characterized. Flexibility, adhesion, and clarity of the UV-curing coating were excellent. UV-curing coatings of aromatic resins were successfully applied to paper packaging such as wine bottle label, plating-aluminum card, and cigarette case.

Keywords: UV-curing technique; UV-curable water-borne polyurethane-acrylate (PUA) resin; UV coatings for paper packaging

Introduction

Due to government regulations and public environmental concerns, coatings formulators and manufacturers are seeking to implement environmentally friendly “green” coating alternatives that perform as well as or better than the conventional solvent-borne systems with mid-to-low solids[1-3]. Additional driving forces in the industry include the increase in cost of solvents, and energy, and the need to reduce CO_2 emission. UV-curing water-borne resin systems have many advantages of low odor, non-toxicity, non-skin irritation and safer production. Therefore, it has become an attractive research and developing areas[4,5]. Radiation curable coatings based on urethane acrylate (UA) oligomers represent the major class of coatings widely used in industry[6-8]. Such coatings are used for protection of articles and objects. In addition, they also fine application as in printing, lithography, and as adhesives. Cured coatings tend to give films a good

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combination of toughness, elasticity and other valuable properties. Study and improvement of properties of urethane acrylate coatings (UAC's) are of permanent interest[9,10]. Although UV curable waterborne coatings based on acrylate functional polyurethane dispersions (UV PUDs) have found acceptance in the wood and resilient flooring markets[11], but the performance of waterborne UV technology may offer potential for other markets as well[12].

In this paper, two kinds of UV-curing water-borne resins were prepared from toluene diisocyanate (TDI)[13]. The reaction conditions were investigated, one-step vs. multi-step synthesis procedure, order of reagent addition, neutralization agent, type of inhibitor and its water-solubility. The bulk performance of the new resin was characterized. Flexibility, adhesion, and clarity of the UV-curing coating were excellent. UV-curing coatings of aromatic resins were successfully applied to paper packaging such as wine bottle label, plating-aluminum card, and cigarette case.

Data of another resin based on aliphatic IPDI monomer will be illustrated in next paper.

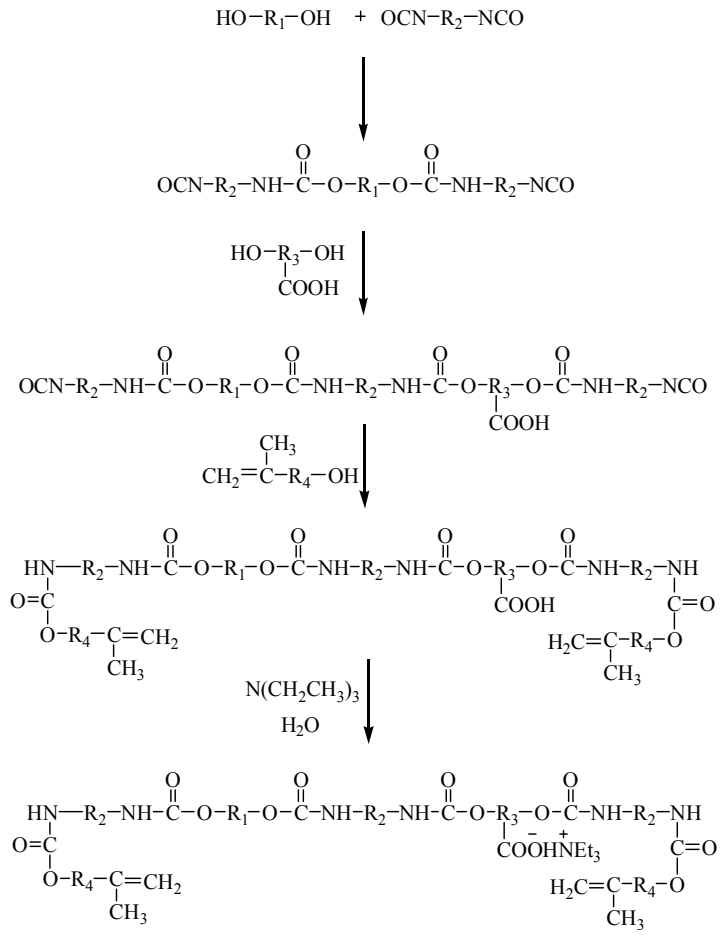
Experimental

Material

The toluene diisocyanate (TDI), isophorone diisocyanate (IPDI) and triethyl amine (TEA) were used as received from Yonghua Fine Chemical Co., Jiangsu, China. Three kind of polyethylene glycol (PEG) with different molecular weight (PEG400, PEG600 and PEG1000). The dimethylolpropionic acid (DMPA) and 1,4-butanediol (BD) were purchased from Guanghua Chemical Co., Shantou, China. 2-Hydroxyethyl methacrylate (HEMA) was supplied from Sartomer Co., PA, USA. HEMA was purified by vacuum distillation before use. Darocur1173 (2-Hydroxy-2-methyl-1-phenyl-1-propanone) and Irgacure2959 (4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl) ketone) were used as an initiator, supplied from Ciba, TEMPO (2,2,6,6-tetramethyl-4-piperidinyl-1-oxy) used as an inhibitor, purchased from Wenzhou Chemical Auxiliary Co., China. All the other chemicals for synthesis were purchased from Shanghai Reagent Co., China. All the above materials were used as received with out further purification.

Synthesis

The UV curable waterborne polyurethane acrylates (UV-WPUAs) was prepared according to the schematic outline shown in scheme 1. A four-necked round bottom flask was equipped with a mechanical stirrer, a thermometer, and a condenser with drying tube. First, TDI was added into the flask with N_2 protection. Then stoichiometric PET600 was slowly dropped in the above reaction vessel by dropping funnel and stirred at 80~90°C for 2~3 hours. Second, the reactor vessel was cooled down below 60 °C, BD and DMPA were slowly added in the above reaction vessel via dropping funnel and stirred at 70~80°C for 2~3 hours. The reactor vessel was again cooled down to 60°C or lower. TEMPO was then added as an inhibitor for the 3.0 ‰ of unsaturated double bonds of the acrylate, HEMA was drop wise added into the above reaction vessel under stirring; reaction temperature was controlled at 60~70°C for 2~3 hours to form the UV-WPUAs prepolymers., In order to control the viscosity of the reaction, the suitable amount of acetone was added as a



Scheme 1 Synthesis Route of the UV-WPUAs resin

diluent during the reaction. Finally, the reaction was complete by adding TEA to neutralize the residual carboxylic groups to the resin over a period of 30 minutes under vigorous stirring. Chain extension continued until -NCO peak (2273 cm^{-1}) and unsatuated double bonds (-CH=CH_2) peak (1637 cm^{-1}) in the FTIR spectrum had completely disappeared as shown in Fig.1.

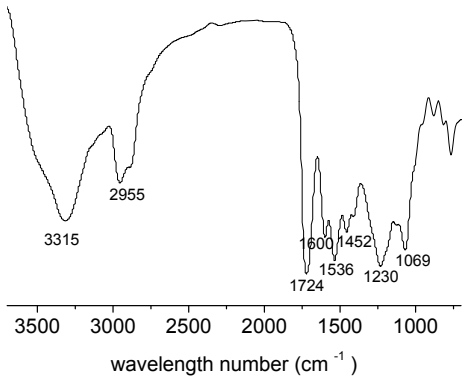


Fig. 1 FTIR spectrum of the UV-WPUAs resin

All the polyurethane acrylates new resin was obtained by evaporating acetone, resulting in a light yellowish viscous liquid (79% solid content).The chemical structure was optimized by the orthogonal experiment, -COOH content, PEG molecular weight, order of reagent addition, type of neutralization agent and neutralizing degree, type of inhibitor and its water-solubility. Influence of initiator's content, dry time and temperature, UV-curing rate were investigated. The bulk property of the resin was characterized.

The orthogonal experiment of the optimizing formulation

According to the demands of the basecoats on the surface of the paper packaging such as wine bottle label, plating-aluminum card, and cigarette case, the optimizing formulation was performed by the orthogonal experiment. The important three factors such as molecular weight of PEG (signal as A), and content of carboxyl group (-COOH) (signal as B)and the content of unsaturated double bonds (-CH=CH_2) (signal as C), was designed by $L_9(3^3)$ orthogonal list with three factors and 3 level such as in Table 1 and 2.

Table 1 Factors of the Orthogonal Experiment

factor / level	A Mn of PEG	B -COOH %	C -CH=CH_2 %
1	A_1 = 400	B_1 = 1 %	C_1 = 1 %
2	A_2 = 600	B_2 = 3 %	C_2 = 3 %
3	A_3 = 1000	B_3 = 5 %	C_3 = 5 %

Table 2 Orthogonal Experimental Design

factor / number	A Mn of PEG	B -COOH %	C -CH=CH_2 %
1	A_1	B_1	C_2
2	A_1	B_2	C_3
3	A_1	B_3	C_1
4	A_2	B_1	C_3
5	A_2	B_2	C_1
6	A_2	B_3	C_2
7	A_3	B_1	C_1
8	A_3	B_2	C_2
9	A_3	B_3	C_3

Characterization of UV-WPUAs resin

The Infrared spectra were recorded on a MAGNA-IR750 (Nicolet Instrument Corporation, USA). The particle ratio of the resin emulsion was measured by microtrac particle size analyzer (Malvern II C, He-Ne type laser with wavelength 633 nm was used) the range of particle size is 0.5~1000 nm. The viscosity of the final products was determined with a NDJ-1 model spinning viscometer (Balance Instrument Co., China) with the speed of 750 rpm. The solubility of the resin in water was investigated by different concentration of 60%, 40%, 20%, 10% and 1% in water at ambient temperature. If the solution is clear, the water solubility of the resin is good. The density of the resin was measured by the gravity bottle with the accuracy of 0.001. The VOC (Volatile organic compounds) of the resin was measured by gas chromatography according to the Chinese National Standard GB/T 6751. The solid content of the resins were obtained by evaporating acetone according to the Chinese National Standard GB/T1725-79. Other properties of the resin were also measured according to the Chinese National Standard respectively.

Preparation of UV curable samples and UV curing

The formulations of all UV curable samples were prepared by adding 5.0 wt% of Darocure2959 as a photoinitiator to above solution of the UV-WPUAs resin, then adding water into the solution to dilute the solid content to 60% from 79%. All samples were coated on the surface of the write paper (Unite, DB, 225 g/m^2) by plate coater or the coil painter with 3~5 μm thickness at room temperature. First, all samples were heated to 80~90°C for 2 hours to remove water, then UV cure on a UV conveyer system with a 2400W high pressure mercury lamp at the transmit rate of 627 cm/min. Curing time was measured by finger-press method.

Results and Discussions

Table 3 bulk property of the UV-WPUAs resin

property	results	methods
Appearance	a light yellowish viscous liquid	GB/T1721-79
Solid content (%)	79.0	GB/T1725-79
pH value	7.0	Fine pH paper
Density (g/mL)	1.15	GB/T6750-86
Colour	2#	GB/T1722-92
Viscosity (mPa·s)	16366	GB/T1723-93
Solubility of water	good	Q/STDN2-2006
Stability of storage	> 6 months	Q/STDN2-2006

Table 4 Design and evaluation of the orthogonal experimental

No.	A	B	C	Water solubility	flexibility	Rate of UV cured	y_i
1	A_1	B_1	C_2	7.0	15.0	21.0	43.0
2	A_1	B_2	C_3	17.5	15.0	35.0	67.5
3	A_1	B_3	C_1	21.0	15.0	7.0	43.0
4	A_2	B_1	C_3	24.5	22.5	35.0	82.0
5	A_2	B_2	C_1	31.5	22.5	14.0	68.0
6	A_2	B_3	C_2	35.0	30.0	35.0	100.0
7	A_3	B_1	C_1	35.0	28.0	7.0	70.0
8	A_3	B_2	C_2	35.0	30.0	14.0	79.0
9	A_3	B_3	C_3	35.0	30.0	35.0	100.0
y_{j1}	153.5	195.0	181.0				
y_{j2}	250.0	214.5	222.0				
y_{j3}	249.0	243.0	249.5				
$\bar{y}_{j1}$	51.2	65.0	60.3	$\sum_{i=1}^{9} yi = 652.5$			
$\bar{y}_{j2}$	83.3	71.5	74.0				
$\bar{y}_{j3}$	83.0	81.0	83.2				
Rj	32.1	16.0	22.9				
Optimum Level	A_2	B_3	C_3	Optimum result A_2 B_3 C_3			
Key factor	A	C	B				

Bulk property of the UV-WPUAs resin

Bulk properties of the UV-WPUAs resin were measured as shown in Table 3. It could be seen that the bulk properties of the resin is excellent with good appearance, high solid content, good water solubility and long stability of storage more than 6 months. Reaction condition and synthetic formulation of the resin very much determined the coating bulk

property. Content of -COOH, and molecular weight of PEG were confirmed by orthogonal experiment. The results of the orthogonal optimization indicated that the synthetic resin had excellent performance when the content of carboxyl group (–COOH) was 3.0 $wt\%$, the content of unsatuated double bonds (-CH=CH_2) was 3.0 $wt\%$, and molecular weight of PEG was 600, which was shown as in Table 4. The optimized results in Table 4 is $A_2B_3C_3$ which depends on the total scope (equal to y_i) summing up by the important three factors such as molecular weight of PEG (A_i), and content of carboxyl group (-COOH) (B_i) and the content of unsaturated double bonds (-CH=CH_2) (C_i), where Y_{ji} is the average value of Yi to evaluate bulk property of UV cured film, and R_j is the grade differential to the average value of Yi.

FT-IR spectrum analysis of the UV-WPUAs resin

The structure of the UV-WPUAs was confirmed by FTIR spectroscopy as shown in Fig1. The spectrum showed that the absorption peaks of typical polyurethane at 3315~3350 cm^{-1}(N-H, hydrogen bond), 2800-2955cm^{-1}(-CH_3 and -CH_2-), 1724 cm^{-1}(C=O), respectively.

The particle ratio of the UV-WPUAs resin

The particle ratio of the resin emulsion was measured by microtrac particle size analyzer. The size distribution and statistics graph by the volume was shown as in Fig. 4 and 5.

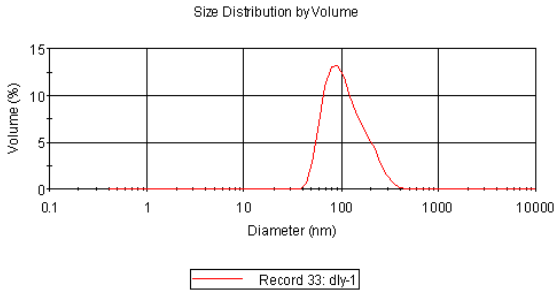


Fig 2 Size distribution of the resin particle in the emulsion by volume

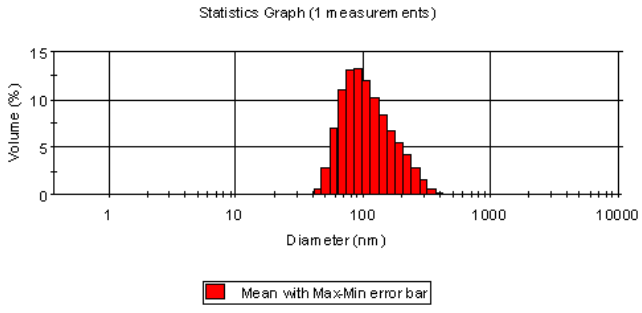


Fig. 3 Static distribution of the resin particle in the emulsion by volume

The result show s that z-Average size of the resin particle in the emulsion is 123.1 nm, the index of size distribution (polydispersity) is 0.117. Generally, the size of the resin

particle is smaller, the stability of the emulsion is longer, and then the water solubility of the resin is better. It could be seen that the water solubility of the resin was measured to be good.

Water soluble character and stability

Water solubility of the UV-WPUAs resin was measured by adding different content of the water and the mixture of water and ethanol (70:30) to dilute the solid content of the resin from 100% to 79.4 %, 68.2 %, 62.3 %, 53.3 %, 43.3 %, 35.4 % and 83.6 %, 67.0 %, 57.0 %, 49.0 %, 45.0 %, respectively. The influence of solid content to viscosity of the resin was shown as in Table 1, Table 2 and Fig.4. The result shows that the water solubility of the UV-WPUAs resin is excellent, and the appearance of the aqueous system is clear during the diluting process shown as in Table 1 and 2. The viscosity of the resin decreased with the solid content decreasing. The mixture of water and ethanol (70:30) is more effective than water alone as diluent.

Table 5 Appearance, solid content and viscosity of the resin by using water as diluent

Solid content (%)	79.4	68.2	62.3	53.3	43.3	35.4
Viscosity (mP·s)	16366	11334	6500	4666	950	536
appearance	clear	clear	clear	clear	clear	clear

Table 6 Appearance, solid content and viscosity of the resin by using the mixture of water and ethanol as diluent

Solid content (%)	83.6	67.0	57.0	49.0	45.0
Viscosity (mP·s)	30541	2406	533	200	97
appearance	clear	clear	clear	clear	clear

When the TEA (triethanol amine) was used as a neutralization agent, the water-solubility of the resin was excellent. TEA was a good neutralization agent since its UV-cured coating could easily absorb water when it is cured. Ammonia was a bad neutralizer, because the water-solubility of the resin was low. With increase hydrophilic groups and neutralization degree, the water-solubility and storage stability of the resin increased; with increase inhibitor level, the storage stability improved. When inhibitor level reached 0.03 *wt%*, The emulsion can stable for more than six months.

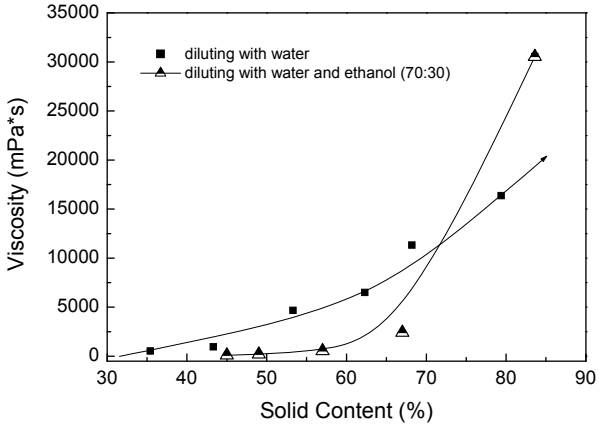


Fig. 4 Influence of solid content to viscosity of UV-WPUA resin

The performance of the UV-curing coatings

Bulk property of the UV-cuing coatings was characterized shown in Table 7.

Table 7 Bulk performance of the UV-cuing coatings

Targeted Performance	Results	Test Methods
Surface tension ≥ 39 mN/m	41 mN/m	Q/STDN1-2005
Good adhesion on paper	pass	3M adhesive tape
Good adhesion on aluminum film	pass	3M adhesive tape
Right folding (90°) ≥ 20 cycles	≥ 30	Q/STDN1-2005
Back folding (180°) ≥ 1 cycle	≥ 10	Q/STDN1-2005
Gloss (20°) ≥ 30	30.5	Q/STDN1-2005
VOC content ≤ 200 ng/m^2	131.7 ng/m^2	Gas Chromatography

The results show that surface tension is 41 mN/m. Higher than targeted 39 mN/m. Adhesion on paper and aluminum is good. The flexibility is excellent, 90° right folding (30 cycles) and 180° back folding (10 cycles) well passes required 20 and 1 cycles, respectively. VOC content is 131.7 ng/m^2, less than the targeted 200 ng/m^2 by Gas Chromatography. The photography of the UV-curing coatings on paper package was shown as in Fig. 5. It clearly indicates that the UV-curing coatings have good appearance, higher gloss, and are suitable for protecting printed surface.

Fig. 5 Paper coated with the UV-cured WPUA coating

Conclusions

Novel water-borne UV-curing polyurethane acrylates (UV-WPUAs) resins were prepared. Content of -COOH, molecular weight of PEG and content of unsaturated double bonds (-CH=CH_2) were confirmed by orthogonal experiment. The results indicated that the synthetic resin had excellent performance when the content of carboxyl group (–COOH) was 3 $wt\%$, the content of unsaturated double bonds (-CH=CH_2) was 3 $wt\%$, and molecular weight of PEG was 600.

The optimal technologic condition, such as order of adding materials, type of neutralization agent, neutralization degree, type of inhibitor and water-solubility were studied. The results show that the optimal technologic condition to synthesis the UV-WPUAs resins is as follows: the temperature of reaction is 80~90°C, and the temperature of food adding is below 60°C, and reaction time of every steps is 2~3 hours. Order of adding materials is First, TDI was added into the flask, and then PET600 was slowly dropped. Second, BD and DMPA were slowly added. Thirdly, HEMA with TEMPO (0.03 *wt%*) was added. Finally, the reaction was complete by adding TEA to neutralize the residual carboxylic groups.

The optimal UV-curing process of the UV-WPUAs resin such as the influences of initiator's content, dry time, dry temperature, inhibitor's content on UV-curing rate were discussed. The formulations of all UV curable samples is 5.0 wt% of Darocure2959 as an initiator, the solid content of the resin is about 60%, the thickness of UV-curable coating was controlled to 3~5 μm. All samples coated were heated to 80~90°C for 2 hours to remove water before UV curing, it is special technique to be need for water-borne UV curable coating.

The bulk performance of UV-curing coatings of the UV-WPUAs resin was appraised. Flexibility, adhesion, and brightness of the UV-curing coatings were excellent. UV-curing coatings of the UV-WPUA resins were successfully applied to the paper of the package such as wine bottle label, the plating-aluminum card, and the cigarette case. It is clear that water-borne UV-curing coatings have potential for various applications.

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