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Preparation and characterization of the heat-resistant UV curable waterborne polyurethane coating modified by bisphenol A

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Abstract. In this study, the modified ultraviolet (UV) curable waterborne polyurethane was obtained from isophorone diisocyanate (IPDI), polyethylene glycol (PEG, MW=600), α,α-dimethylol propionic acid (DMPA), hydroxyethyl acrylate (HEA) and bisphenol A. The rigid moiety was introduced into the main chain of polyurethane to improve its heat-resistance. The copolymer structure was confirmed by Fourier transform infrared spectroscopy (FT-IR). Thermal property and UV curable behavior of the coatings were investigated. The glass transition temperature (T_g) of the modified film was determined by differential scanning calorimetry (DSC). Thermal gravimetric analysis (TGA) was employed to investigate the thermal stability of the modified film. The results show that the average particle diameters increased from 69.25 to 95.12 μm as the content of bisphenol A increased from 0.00 to 9.25%. The optimum bisphenol A dosage was 7.23% (wt%), the T_g of the modified film increased by 7.07°C and 5% weight-loss temperature (233°C) increased by 14°C. The optimum irradiation time was 10–20 minutes after the coatings being painted on an armor plate at room temperature and initiator dosage was 5% (wt%) of the latex.

Keywords: *coatings, waterborne polyurethane, bisphenol A, modification, heat-resistant*

1. Introduction

Recently, environmental legislation is increasingly strict with coatings industry. The coatings technology is changed from traditional solvent-borne coatings to environmental friendly coatings [1]. Waterborne coatings are new safe materials that can reduce environmental pollution [2]. Because of the virtues in environmental protection, waterborne coatings which were rapidly developed in the past few years have been paid more and more attention and expected to substitute the solvent coatings. But the waterborne coatings are inferior to the solvent coatings for their low chemical resistance, scratch resistance and slow solidification [3]. Although ultraviolet (UV) radiation is a well-accepted technology for the fast curing of polymeric materials, the UV curable coatings have odor, emission monomers and are not zero-VOC emission [4]. Therefore, in order to overcome above disadvantages, UV curable waterborne coating is generated. Presently, because of many merits, including nonflammable, non-toxic, friendly environment, fast solidification, resistance to organic solvents and excellent mechanical properties [5–8], UV curable waterborne polyurethane coatings (UVWPU) have received more and more attention in the past few

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years and their development has resulted in a wide variety of technical approaches in industrial applications, such as fast drying protective coatings, printing inks and adhesives [9, 10]. But they have some inferior properties such as low heat resistance and weak tensile strength when the external temperature exceeds 80°C [11]. Thus, the heat resistance of the UVWPU was improved by several scholars. The conventional method of preparing the heat resistance UV curable waterborne coatings is by way of synthesizing hyperbranched polymer introducing the vinyl groups into the polyurethane chains. For example, Xiong *et al.* [12] synthesized dendritic poly(urethane acrylate) by using 2,4-toluidene diisocyanate, β-hydroxyethyl arcylate, glycidyl methacrylate and polyol under the condition of the thermal degradation temperature of 208°C. It is well known that the thermal degradation of polyurethane contains two steps and the first one is related to the hard segments [13]. However, the heat resistance of the film was improved by synthesizing special hard segment [14].

Therefore, in this article, a series of novel modified polymers of UVWPU are prepared in three steps. Firstly, the preparation of UVWPU prepolymer is synthesized from isophorone diisocyanate (IPDI), polyethylene glycol (PEG, MW=600), 2,2-dimethylol propionic acid (DMPA). Secondly, the UVWPU chain is extended by bisphenol A. finally, the polyurethane main chain is end capped with hydroxyethyl acrylate (HEA), neutralized with triethylamine (TEA) and dispersed with deionized water. The rigid moiety is introduced into the polyurethane molecule by using bisphenol A to improve the thermal properties of coating.

At present, the particle size of the modified UVWPU dispersions was investigated by Microtrac S3500 (Microtrac Montgomeryville, PA, USA). The structure and properties of the modified film were studied by several techniques such as FT-IR (Fourier transform infrared spectroscopy), DSC (differential scanning calorimetry) and TGA. The results show that the modified film has a good heat-resistance.

2. Materials and methods

2.1. Materials

IPDI (pure grade, 98%) was purchased from Alfa Aesar (Massachusetts, USA) and used without further purification. Dibutyltin dilaurate (pure grade 90%) was supplied by Energy Chemical (Shanghai, China) as a catalyst. PEG600 (AR) was produced by Shanghai Sangon Biological Engineering Technology and Services Co., Ltd. (Shanghai, China) which was dried for 5 h at 105°C in the vacuum oven before use. DMPA (pure grade 99%) was obtained from Alfa Aesar (Massachusetts, USA), which was purified and dried at 105°C for 4 h in the vacuum oven. Triethylamine (TEA) and acetone (AR) were obtained from Fuyu (Tianjing) Industry of Fine Chemicals Co., Ltd. (Tianjing, China), which were dried for one week with 4 Å molecular sieves (AR, Shanghai Zeolite Molecular Sieve Co., Ltd, China) before use. 2-hydroxyl-2-methylpropiophenone (pure grade, 97%) was supplied by Sigma Aldrich Inc. (Shanghai, China). HEA (pure grade 97%) was supplied by Energy Chemical (Shanghai, China). Bisphenol A (pure grade 99%) was supplied by Bio Basic Inc. (Toronto, Canada). HEA and bisphenol A were used without further purification.

2.2. Preparation of aqueous dispersion

The preparing process of dispersion is shown in Figure 1. The synthesis was carried out in a four-necked, round-bottomed flask equipped with mechanical stirrer, dropping funnel, nitrogen protector and reflux condenser with a drying tube. The reaction temperature was controlled by using a constant-temperature oil bath. Firstly, IPDI, PEG600, and DMPA were added with suitable mole ratio. Then, dibutyltin dilaurate was added into the flask under moderate stirring. The reaction was conducted at 85°C until the theoretical –NCO group content reached. Then, the bisphenol A was added into the system and reacted at 75°C for 2 h. Thereafter the HEA and catalyst were added into the system and reacted at 75°C. The end point of reaction was determined by the disappearance of –NCO stretching peak through infrared (IR) spectroscopy. The acetone was added into the flask to adjust the viscosity of the solution in course of reaction. When the reaction was completed, the reaction system was cooled down to 25°C and the neutralizing agent (TEA) was added and stirred for 30 minutes. The aqueous dispersion was obtained by adding deionized water as the dispersion medium to the reaction system under vigorous stirring. The UV

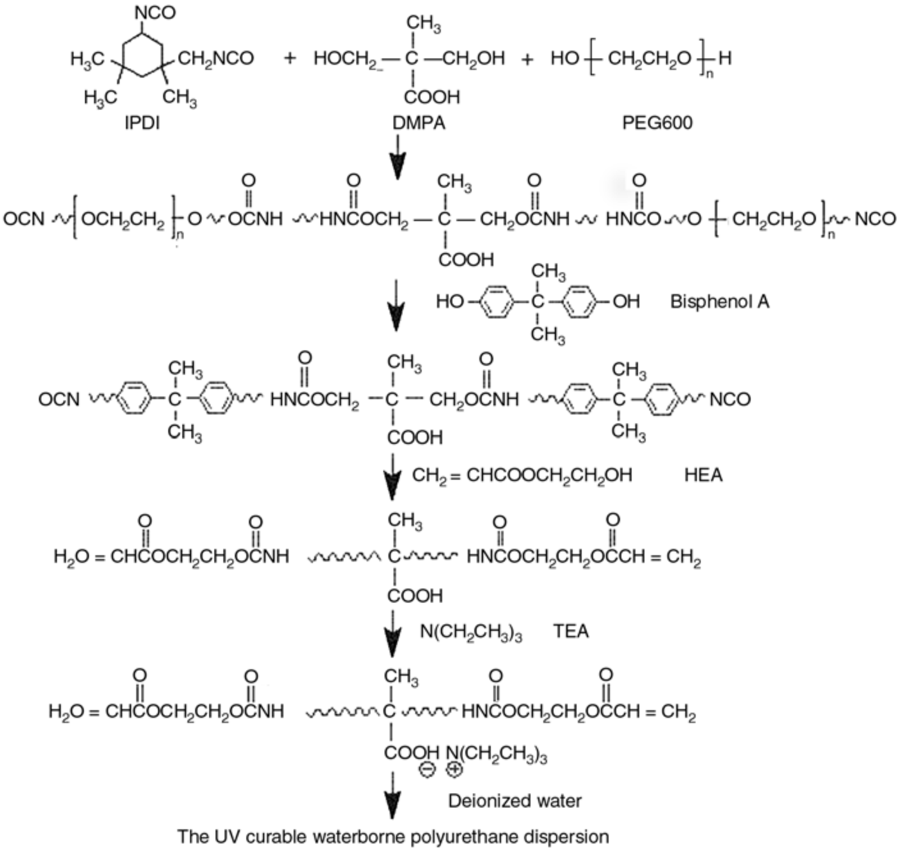

Figure 1. The preparation process of the UVWPU dispersion

curable waterborne polyurethane dispersion (solid content 25%) was obtained after removal of the acetone from the reaction system by rotary vacuum evaporation.

The varying content of –NCO during the reaction was determined by the di-*n*-butylamine back titration method. The theoretical value of –NCO was calculated by Equation (1) [5]:

$$\mathrm{NCO}\,[\%] = \frac{(M_{\mathrm{NCO}} - M_{\mathrm{OH}})\cdot 42}{W_{\mathrm{NCO}} + W_{\mathrm{OH}}}\cdot 100 \qquad (1)$$

where M_{NCO} was the mole number of NCO group in the system. M_{OH} was the mole number of OH group. W_{NCO} was the weight of diisocyanate. W_{OH} was the weight of alcohols.

2.3. Preparation of UV cured films

The UVWPU films were formed by irradiating with UV mercury lamp (15 W) in the period of time with suitable photoinitiator 2-hydroxyl-2-methylpropiophenone based on the resins onto an armor plate at room temperature and followed by drying the film 48 h at room temperature after water was evaporated until reaching a constant weight before test.

2.4. Characterization and measurements

2.4.1. IR analysis

The infrared (IR) spectra were recorded with a Fourier transform infrared spectroscopy (FT-IR) instrument in the 400–4000 cm^{-1} region. Samples were coated directly on to the surface of a KBr crystal, respectively, and measured after film forming and drying.

2.4.2. Particle sizes and distributions

The particle size distributions of the dispersion were measured by using the Microtrac S3500 (Microtrac Inc., Montgomeryville, PA, USA) laser light particle size analysis apparatus. Samples were diluted with water into an appropriate concentration as indicated by the instrument. Test temperature: 25°C.

2.4.3. TGA analysis

The TGA of the UVWPU films were carried out on a Model ZRY-2P (Shanghai Precision and Scientific Instrument Co., Ltd., China) thermal analyzer and the samples were placed in a platinum sample pan and characterized by performing a scan from 50 to 700°C at heating rate of 10°C/min in N_2 atmosphere.

2.4.4. DSC analysis

The T_g of UV cured films is evaluated by Mettler DSC1 (Mettler Toledo, Switzerland) thermal analyzer at temperatures from –100 to 250°C and 10°C/min heating rate in N_2 atmosphere.

2.4.5. Gel contents of the film

The ultraviolet curable behaviors of UVWPU were detected in gel content. The gel ratio (G) of the UVWPU specimen was tested by immersing the UVWPU films in acetone at 48 h and was calculated by Equation (2) [15, 16]:

$$G = \frac{M_1}{M_2} \cdot 100 \qquad (2)$$

where M_2 and M_1 are the weight of UVWPU film before and after purification, respectively.

3. Results and Discussion

3.1. IR Analysis

The structure of the UVWPU was confirmed by FT-IR as shown in Figure 2. The typical absorption peaks of polyurethane could be seen from the figure at 3310–3360 cm^{-1} (NH stretching vibration), 2850–2950 cm^{-1} ($-CH_2$ stretching vibration), 1714 cm^{-1} (C=O stretching vibration), 1615 cm^{-1} ($-C_6H_5$ stretching vibration), 1540 cm^{-1} (NH deformation vibration), 1461 cm^{-1} ($-CH_2$ deformation vibration) and 1124 cm^{-1} (C–O–C stretching vibration), respectively. The –NCO absorption appeared at 2265 cm^{-1} for prepolymer and disappeared for the product which indicated that –NCO groups had been blocked for the product. The $-C_6H_5$ absorption appeared at 1615 cm^{-1} for polymer after chain extension which indicated that bisphenol A had been introduced into the main chain of the polyurethane. The spectrum of the product obviously showed the absorption peaks at 1631 cm^{-1} (C=C stretching vibration), which demonstrated that the C=C bond had been incorporated in the polyurethane chains. In addition, the spectra of UVWPU film displayed that the C=C bond decreased significantly after UV radiation, which illustrated that the C=C bond of the polyurethane chains has been polymerized.

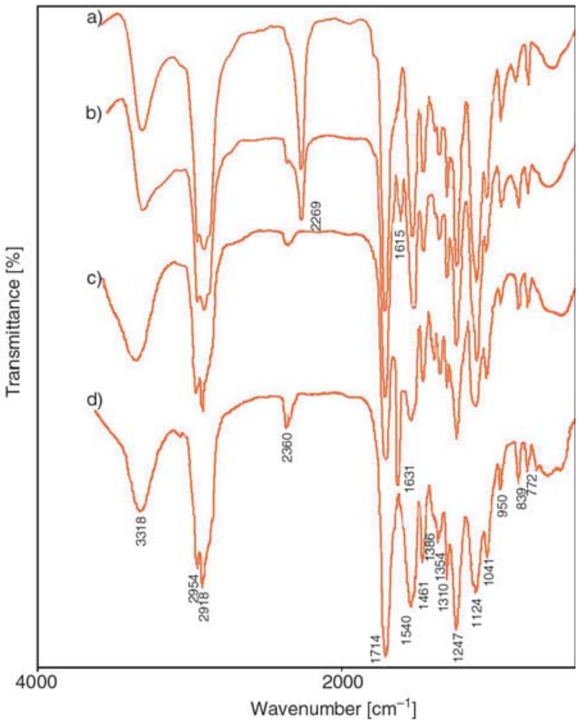

Figure 2. The FT-IR spectra of the modified UVWPU: a) prepolymer, b) polymer after chain extension, c) end-capping polymer, d) cured film)

3.2. Average particle size of the UVWPU dispersions

It is well known that the average particle size and dispersibility of the UVWPU are governed by several factors such as the hydrophilicity, prepolymer viscosity, ionic group position, chain rigidity, etc. [17, 18]. In this study, the molar ratio of –NCO/ –OH, the mass ration of DMPA, HEA and PEG are fixed to a number separately. We have synthesized a series of UVWPU with different content of the bisphenol A. The average particle diameters of the UVWPU dispersions are shown in Figure 3. The average particle diameters of the suspension are mainly affected by the mass ration of bisphenol A and DMPA. Figure 3 and Table 1 show the content of DMPA in the main chain decrease and the dilution stability of the suspension becomes worse as the content of bisphenol A increased from 0.00 to 9.25%, and the average particle diameters increased from 69.25 to 95.12 µm obviously, the reason of which was the decreasing of the hydrophilicity content of the chains and the increased chain rigidity after using bisphenol A as the chain extender.

Table 1. Suspension stability of the UVWPUs at different content of DMPA

Bisphenol A content [wt%]	DMPA content [wt%]	Centrifugal[a]		Dilute stability[b]
		Before	After	
0.00	9.93	Translucence	Translucence	Translucence
2.67	9.42	Translucence	Translucence	Translucence
5.06	8.92	Translucence	Translucence	Translucence
7.23	8.50	Translucence	Translucence	Flocculation
9.25	8.10	Translucence	Translucence	Delamination, flocculation

[a]Rev: 3000 r/min, time: 15 min

[b]Latex was diluted with adding deionized water (solid content of the diluted latex, 3%) and deposited 48 h before observing experimentally

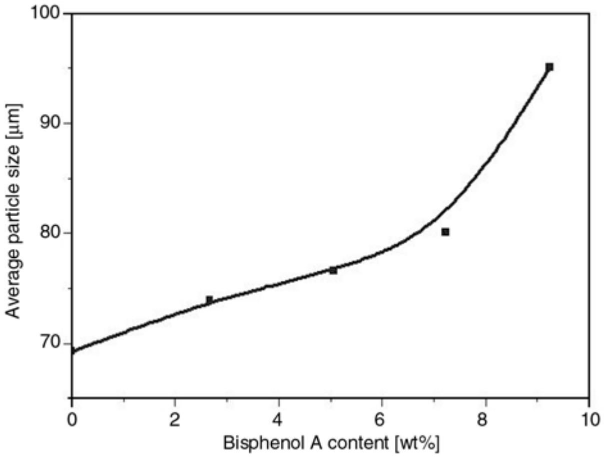

Figure 3. Effect of the bisphenol A content [wt%] on the latex average particle size

The experiment result of the suspension stability is shown in Table 1.

3.3. Thermal properties

In this study, heat-resistance of the UVWPU film with different content of the bisphenol A is measured according to GB 1735-79 (Table 2). The date of the Table 2 displayed that the heat-resistance of the UVWPU film without bisphenol A is bad, but the heat-resistance of the UVWPU film is increased with the addition of the bisphenol A as chain extender gradually increasing from 0.00 to 7.23%. In our study, we found that the UVWPU film is the best heat-resistance during the content of the bisphenol A at 7.23%. The explanation of this fact is that the chain rigidity is increased and the cross-linking density is decreased which is due to the fact that the content of HEA of system decreases as the content of bisphenol A increased from 0.00 to 9.25%. When the content of bisphenol A exceeds 7.23%, the heat-resistance is decreased by the reduction of the cross-link density.

The TGA curves of the unmodified film and the modified film (content of bisphenol A at 7.23%) are shown in Figure 4. The results showed that the sample UVWPU without bisphenol A had lower initial thermal decomposition temperature than that with bisphenol A as the chain extender. The results of TGA for the modified film obviously indicated the 5% weight-loss temperature of the modified film at 233°C, which was improved by 14°C than

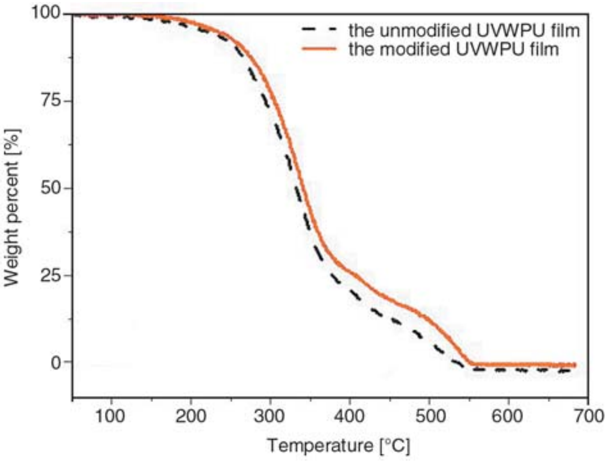

Figure 4. The TGA curves of the UVWPU films at the heating rate of 10°C/min

Table 2. Thermal properties of UVWPU films at different content of bisphenol A

Bipsphenol A content [wt%]	Thermal properties of UVWPU films[a]				
	80°C	90°C	100°C	110°C	120°C
0.00	Acceptance	Below grade	–	–	–
2.67	Acceptance	Acceptance	Acceptance	Below grade	–
5.06	Acceptance	Acceptance	Acceptance	Below grade	–
7.23	Acceptance	Acceptance	Acceptance	Acceptance	Below grade
9.25	Acceptance	Acceptance	Acceptance	Below grade	–

[a]Test time is 2 h, acceptance means the film without color change , crinkle, desquamate, dehisce and frothy

the UVWPU without using bisphenol A. In several studies, it has been concluded that the first and second stages of degradation of polyurethane copolymers are related to the degradations of the hard and soft segments, respectively [11]. The UVWPU polymer coating film in the TGA test presents two stages of degradation associated with the degradations of urethane hard segments and PEG600 soft segment. The unmodified film exhibits lower temperature of 5% weight loss due to the high aliphatic chain of hard segments. Notably, the urethane groups of the modified film after benzene ring incorporating in hard segment decompose at higher temperature than the urethane groups of the unmodified film, implying that the degradation of urethane groups of the modified film is hindered by the aromatic chains.

The DSC curves of the unmodified UVWPU film and the modified UVWPU film (content of bisphenol A at 7.23%) are shown in Figure 5.

Figure 5 showed that the unmodified UVWPU film was observed only one T_g at 34.86°C, which is lower than that of the modified UVWPU film (dosage of bisphenol A at 7.23%) and the T_g of the modified film increased by 7.07°C (about 41.93°C). The explanation is that the chain rigidity is introduced by using bisphenol A as the chain extender, the chain movement is confined, which increases the T_g value. But we can observe a weak peak (139.50°C) in the DSC curve of the modified film, which might be due to the evaporation of water. The UVWPU film with only one T_g might be due to the chain high cross-linking density which was formed by irradiating with UV mercury lamp. In addition, the soft-segment and hard-segment have nicer compatibility.

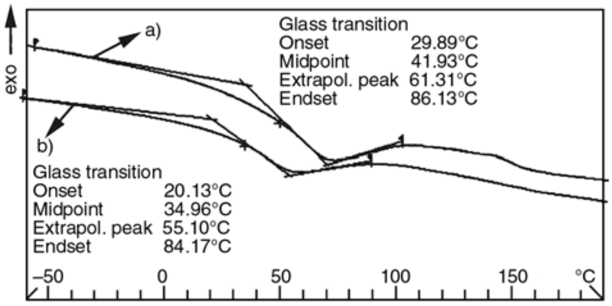

Figure 5. The DSC curve of the films at the heating rate of 10°C/min: a) the modified UVWPU film, b) the unmodified UVWPU film

3.4. Ultraviolet curable behaviors

The most important parameter for the UV curing process is the gel rate. In this study, the contents of initiator (4%) and the content of bisphenol A (7.23%) are fixed separately. We have investigated the effect of different drying times before irradiation on the UV curing process (Figure 6). Figure 6 shows that the sample with drying time at 20 min exhibits the highest gel rate and the curing rate of the modified UVWPU film increases with the increasing of irradiation time at the beginning of irradiation before reaching a constant value. It can also be seen from Figure 6 that the curing rate presents the different variation tendency and increases rapidly. Comparing the sample curve with drying time at 10 min to that at 20 min, we find that the curing rate of the former approaches to that of latter and the curing process is absolutely accomplished after 30 min. Reason for this is the higher water content at the beginning of the irradiation and the low concentration of active center and the curing rate. Therefore, the optimum irradiation time is the 10–20 min after the resins onto an armor plate at room temperature.

There is the optimum initiator content in the specifically system. In this study, the content of bisphenol A (7.23%) is a fixed number. We have investigated the effect of initiator content on the UV curing process (Figure 7). Comparing the sample with initiator contents at 4 and 6%, Figure 7 shows that the highest gel ratio of sample happens at an initiator content of 5%, which is caused by the lower energy utilization rate and active center con-

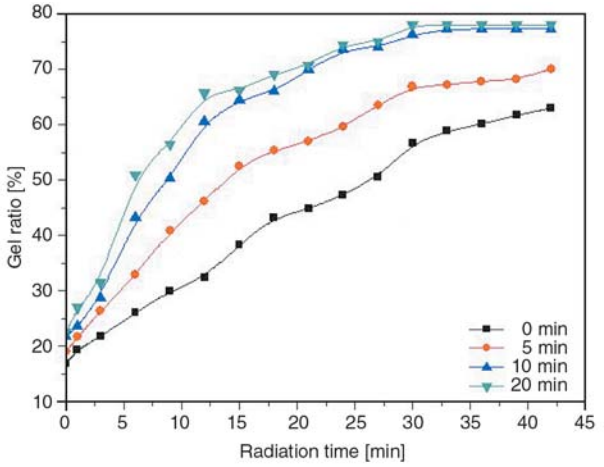

Figure 6. Relationship between the gel ratio for different drying time and the radiation time

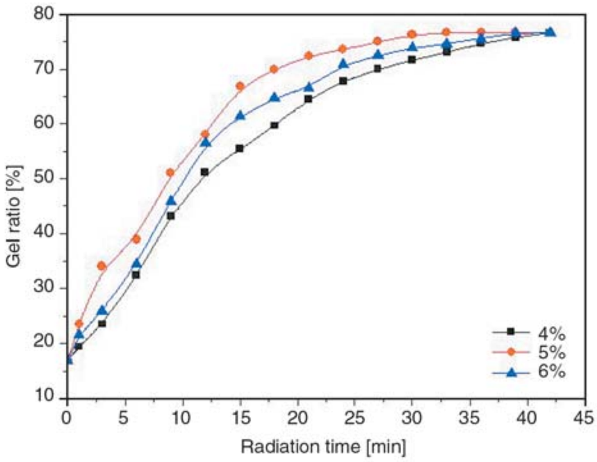

Figure 7. Relationship between the gel ratio for different initiator content and the photo-irradiation time

centration when the initiator content was low. On the other hand, the active center concentration increases with the increasing of the initiator content, which results in the chain termination in superfluous active center coupling each other [19]. Therefore, it can be revealed that the optimum initiator content is 5%.

4. Conclusions

We have successfully synthesized the novel ultraviolet curable waterborne polyurethane coating by introducing the rigid moiety into the main chain of the polyurethane using bisphenol A as chain extender. The results showed that the optimum bisphenol A dosage was 7.23% (wt%), the average particle diameters increased from 69.25 to 95.12 μm as the content of bisphenol A increased from 0.00 to 9.25%. Comparing with the unmodified UVWPU, the obvious advantage of heat resistance of modified UVWPU film was displayed after the rigid chain was introduced into the polyurethane main chain. Otherwise, the T_g of the modified UVWPU was 41.93°C which increased by 7.07°C and the 5% weight-loss temperature (233°C) of the modified UVWPU film increased by 14°C. The curing process indicated that the optimum irradiation time was 10–20 min after the resins onto an armor plate at room temperature and initiator content was 5%.

Acknowledgements

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