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Study on Synthesis and Thermal Stability of Non-amine Waterborne Polyurethane-polyacrylate

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Abstract

In order to satisfy the low VOC and temperature resistance of coating requirements in cigarette printing industry. Waterborne polyurethane polyacrylate emulsion (WPUA) was synthesized with thermotolerant polyester diol (NCL), 4,4'-dicyclohexyl methane diisocyanate (HMDI) and methyl methacrylate (MMA) as raw materials, using both carboxylic acid and sulfonate as hydrophilic chain extender agent. WPUA with zero VOC and no triethylamine was prepared by solvent-free method to meet the requirements of cigarette packaging industry. The WPUA emulsions and films were characterized by FT-IR, transmission electron microscope (TEM), particle size analysis and thermogravimetric analysis (TGA). The effects of different kinds of isocyanates, polyalcohol and chain extender on thermal stability of the WPUA films were investigated. The results showed that the average particle size of the emulsion was reduced due to the addition of aliphatic diamine sulphonate (AAS). TGA results showed that the decomposition temperature of WPUA film synthesized by NCL, HMDI and novel chain extender hydroquinone bis(β-ethyl) ether (HQEE) was higher than that of WPUA film synthesized by polycaprolactone diol (PCL), isophorone diisocyanate (IPDI) and 1,4-Butanediol (BDO), the decomposition temperature increased by 60.96 °C, 69.37 °C, 139.70 °C when the mass loss rate of WPUA film was 20%, 30%, 50%. And glass transition temperature (Tg) of polyurethane increased with the enhancement of the symmetry and rigidity of molecules.

Key Words: Polyurethane-polyacrylate, Emulsion Polymerization, Thermal Stability, Heat Resistance

1. Introduction

Waterborne polyurethane (WPU) is a block copolymer made of flexible soft segments and rigid hard segments, the soft segment includes macromolecular polyols (polyester or polyester polyols), and the hard segments includes polyisocyanates and small molecule chain extenders [1]. The properties of the polyurethane are determined by the chemical structure, composition, relative content, length of the segment, the distribution of the segments and the degree of crosslinking in the soft and hard segments of the molecular chain. Therefore, the soft segment and hard segment structure of polyurethane have a direct or indirect effect on the performance of waterborne polyurethane. By adjusting the structure and proportion of water-based polyurethane soft and hard segments, the products with different performance could be designed according to the needs of the market [2]. Compared with solvent-based polyurethane, waterborne polyurethane (WPU) has the advantages of non-toxic, non-pollution, etc. Therefore, as one of the main environmental-friendly waterborne coatings, waterborne polyurethane has attracted people's attention for its development [3]. The WPU studied in this paper is mainly used for the print-

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ing, decoration, coating and protective coating of aluminum foil, aluminum foil composite, transfer paper packaging materials such as tobacco, wine, food and medicine. If traditional solvent-based polyurethane was used by packaging industry, it will have a lot of volatile organic solvents which will pollute the environment, and the solvent remaining on the wrapping paper is harmful to human health [4,5]. Therefore, the volatile organic compounds (VOC) value of cigarette packaging paper should be satisfied with the industry standard requirements, zero VOC packaging materials will become one of the hotspots in the research field. Generally the service temperature of cigarette printing coating should be more than 140 °C. However, some of the products on the market only have temperature resistance at a temperature of 100 °C to 120 °C [6]. The development of high temperature resistant WPU with zero VOC has become one of the hotspots in the research field of polyurethane (PU).

In this article, a high temperature resistant nano-core-shell WPUA emulsion was prepared by emulsion polymerization using high temperature resistant polyester diol (NCL), 4,4′-dicyclohexylmethane diisocyanate (HMDI) and methyl methacrylate (MMA) as main raw materials. This paper synthesizes WPUA with zero VOC, no triethylamine, with high temperature resistance, meeting the cigarette packaging industry and environmental protection needs. WPUA synthesized in this paper is an environment-friendly water-based coating suitable for cigarette packaging industry.

2. Experimental

2.1 Materials

Thermotolerant polyester diol (NCL Mn = 2000) was obtained from Qingdao Xinyutian Chemical Co. Ltd, China. polycaprolactone diol (PCL Mn = 1000) was purchased from Qingdao Runcang Chemical Co. Ltd, China. NCL and PCL was dried and degassed at 80 °C under vacuum for 3 h. Isophorone diisocyanate (IPDI) was purchased from Bayer, Germany. 4,4’-dicyclohexyl methane diisocyanate (HMDI) was purchased from Yantai Wanhua chemical group Limited by Share Ltd, China. IPDI and HMDI were vacuum distilled before use. Dimethylolbutanoic acid (DMBA), trimethylol propane (TMP) and dibutyltin dilaurate (DBTDL) were purchased from Sigma-Aldrich, USA. DMBA and TMP was dried at 50 °C for 48 h in vacuum oven. 1,4-butanediol (BDO), methyl methacrylate (MMA) and hydroxyethyl acrylate (HEA) was obtained from Tianjin chemical reagent six factory, China. Potassium persulfate (KPS), chemically pure, was obtained from Tianjin Kermel Chemical Reagent Co. Ltd, China. Sodium hydroxide (NaOH) was obtained from Beijing Chemicals, China. 2-[(2-aminoethyl)amino]-ethanesulfonic acid monosodium salt (AAS) was obtained from Hengzhou City Rui Erfeng Chemical Co. Ltd, China. Hydroquinone bis(β-ethyl) ether (HQEE) was obtained from Qingdao Jade New Material Technology, China.

2.2 Preparation of Waterborne Polyurethane-polyacrylate (WPUA)

A 500 mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer and condenser with drying tube was used as reactor. The reaction was carried out in a constant temperature oil bath. IPDI, NCL and “similar solvent” MMA were mixed and the reation mixture was subsequently the presence of DBTDL for 2 h at 60 °C to obtain NCO-terminated prepolymer. In the second step, BDO, DMBA, TMP and DBTDL were added into the flask and reacted for 2 h at 60 °C. In the third step, HEA was fed into the flask and mixed thoroughly for 1 h. In the fourth step, AAS, NaOH and water were added dropwise at a constant flow rate with high speed stirring, after all of the water had been dropped into the flask, anionic blocked waterborne polyurethane was obtained. Finally, the initiator KPS solution was added dropwise at 75 °C for 1 h, and the reaction lasted for 2 h. The reaction scheme of WPUA is shown in Figure 1. The ratio of reaction for aqueous polyurethane is shown in Table 1.

3. Preparation and Characterization

3.1 Preparation of films

The prepared emulsion was casted on the polytetrafluoroethylene plate, naturally dried for three days, then placed in a drying oven at 60 °C for 24 h. After demoulding, the films were stored in a desiccator [7].

3.2 Characterization

The FT-IR spectroscopy of the film was analysed by

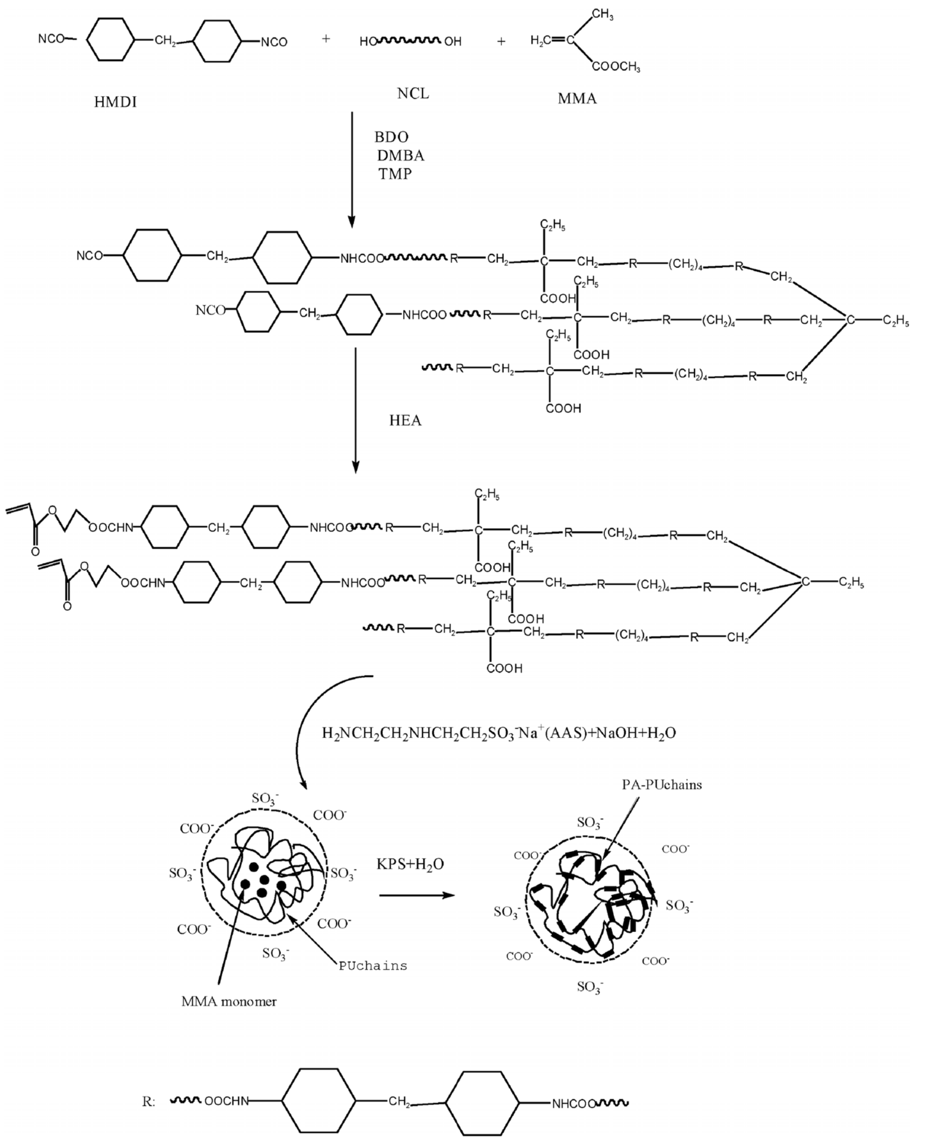

Figure 1. The reaction equation of the waterborne polyurethane-polyacrylate.

Table 1. The ratio of reaction for aqueous polyurethane

Sample	NCL/mol	PCL/mol	IPDI/mol	DMBA/mol	HMDI/mol	BDO/mol	HQEE/mol	MMA/mol	AAS/mol
WPUA1	0	0.005	0.054	0.017	0	0.005	0	0.18	0
WPUA2	0	0.005	0.054	0.017	0	0.005	0	0.18	0.013
WPUA3	0.005	0	0.054	0.017	0	0.005	0	0.18	0.013
WPUA4	0.005	0	0	0.017	0.054	0.005	0	0.18	0.013
WPUA5	0.005	0	0	0.017	0.054	0	0.005	0.18	0.013
WPUA6	0.005	0	0.054	0.017	0	0.005	0	0.18	0

the potassium bromide coating method using VECTOR-22 type Fourier transform infrared spectrometer (BRUKER Co. Ltd, German), the scanning area ranges from 500 cm^{-1} to 4000 cm^{-1}. TGA Q500 (TA instrument, USA) was used to measure the thermostability of the polyurethane films. The samples with a weight of 15~20 mg were heated from room temperature to 600 °C at a rate of 10 °C/min in N_2 atmosphere. DSC-Q2000 (TA instrument, USA) was used to measure the glass transition temperature (Tg). Aluminum pans containing 10 ± 1 mg of samples were subjected to the heating/cooling cycle between -50 and 250 °C under a nitrogen atmosphere (flow rate: 20 mL/min) and the heating rate was 10 °C/min. From the heating run, the Tg of the samples was obtained. The samples emulsion was diluted to a solid mass fraction of about 0.1% and the morphology of the emulsion stained with phosphotungstic acid was determined by transmission electron microscopy (TEM) at H-600 (HITA-CHI instrument, Japan). Zetasizer NANO-ZS9 (Malvern instrument, UK) was used to measure the particle size of the WPUA. All WPUA emulsion were diluted to a mass fraction of about 1%, followed by ultrasonic wave treatment to homogenize the emulsion.

3.3 Property Tests of WPUA Coating

Test the high temperature performance of WPUA coatings: firstly the WPUA paint was attached to aluminum foil paper, then fold the face with WPUA paint over, cut into 10 cm × 10 cm square, put it in an oven at 70 °C and place a 5 kg weight on it for 2 hours. Finally the coating is taken out to observe whether it is stuck together or not [8].

Flexibility and adhesion testing: fold and open the painted aluminum foil, test its flexibility and observe whether the color is broken. The 3M scotch tape attached to the painted aluminum foil paper, and then quickly after the uniform force to peel the tape, and finally observe the surface of the membrane state, test its adhesion.

Gloss of WPUA coatings was tested according to GB/T9754-1979.

4. Results and Discussion

4.1 The FT-IR Spectrums Analysis of WPUA

FT-IR spectroscopy was used to confirm the variety of chemical functionalities present in the polymer matrix. The FT-IR spectra of the prepolymer (PreWPUA) and the waterborne polyurethane acrylate (WPUA) film are shown in Figure 2. As the figure shows, the absorption peak at 3350 cm^{-1} is stretch vibration of N-H and peak at 1540 cm^{-1} is attributed to band vibration of N-H. The absorption peak at 2980~2850 cm^{-1} are associated to C-H stretch of $-CH_3$, $-CH_2$ and -CH. The characteristic absorption peak at 1730 cm^{-1} is the C=O carbonyl stretchings of urethane. The characteristic absorption peaks of isocyanate bonds generally appear between 2200 cm^{-1} and 2300 cm^{-1}. Compared PreWPUA with WPUA, the vibration peak of WPUA at 2210 cm^{-1} can be clearly seen to disappear, this indicates that the -NCO group has reacted with the -OH group by nucleophilic addition to form a carbamate group (-NHCOO-) in the synthesis process, and there is no free -NCO groups in the synthesized WPUA emulsion.

4.2 Morphology Analysis of WPUA

The morphology of WPUA emulsion particles were observed by transmission electron microscope, the TEM photograph of WPUA1 emulsions without AAS is shown in Figure 3(a) and Figure 3(c), the TEM photograph of WPUA2 with is shown in Figure 3(b) and Figure 3(d). Compared Figure 3(a) with Figure 3(b), it can be seen that WPUA2 emulsion dispersion is more uniform. The hydrophilic groups in the molecular chain are advantageous in dispersing the polyurethane prepolymer in water [9], so WPUA2 emulsion with AAS is well dispersed. Compared Figure 3(c) with Figure 3(d), it is clearly seen that the two figures proved the composite emulsion has core-shell structure, which is mainly due to the different electron density of core layer and shell. As is shown in the picture, the lighter part is the core layer polyacrylate, and the darker part shows the shell polyurethane [10].

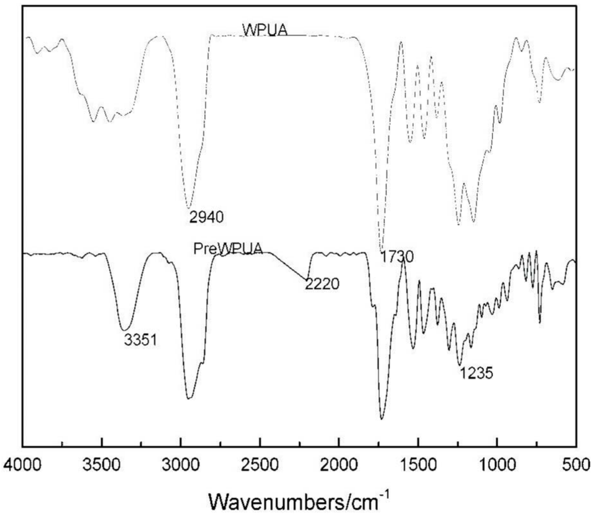

Figure 2. The FT-IR spectra of WPUA and prepolymer.

4.3 Particle Size Analysis of WPUA

The particle size and distribution of WPUA1 emulsion synthesized by PCL without AAS and that of WPUA2 emulsion synthesized by PCL with AAS were shown in Figure 4(A). And the particle size and distribution of WPUA6 emulsion synthesized by NCL without AAS and that of WPUA3 emulsion synthesized by NCL with AAS were shown in Figure 4(B). As is shown in the Figure 4, the AAS molecule was introduced into the WPUA macromolecule chain by the reaction of $-NH_2$ of the AAS molecule with the -NCO on the polyurethane chain. At the same time, sulfonic groups in AAS molecule has strong hydrophilicity, so the hydrophilicity of WPUA was improved by adding AAS, and dispersion of WPUA in water was improved. The results showed that adding AAS was advantage for reducing the particle size.

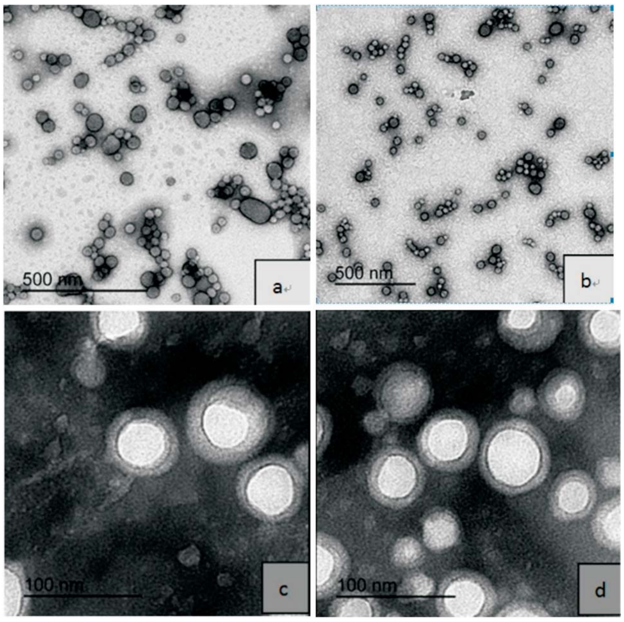

Figure 3. TEM photographs of WPUA. (a, c) WPUA emulsions without AAS; (b, d) WPUA emulsions with AAS.

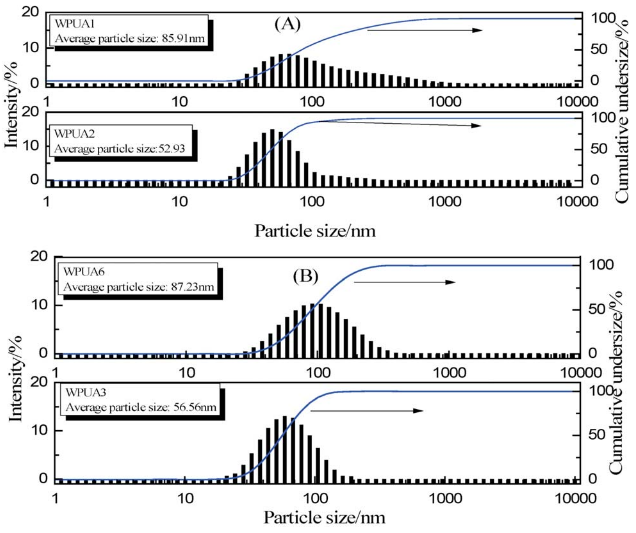

Figure 4. Particle size and distribution of WPUA emulsion.

5. Thermogravimetric Analysis of the WPUA Films

5.1 Thermal Stability of WPUA Films with Different Kinds of Poly Diols

Thermal stability of the WPU films with different kinds of poly diols were shown in Figure 5. It was found from Figure 8 that the thermal stability of WPUA3 film synthesized by NCL was better than that of WPUA3 film synthesized by PCL. Decomposition temperature of WPUA films with different kinds of poly diols were shown in Table 2. The results showed that the decomposition temperature of WPUA3 film was higher than that of WPUA2 film by 20.24 °C, 32.14 °C, 100.86°C, when the mass loss rate is 20%, 30%, 50%. NCL was made by polycondensation of sebacic acid, isophthalic acid, ethylene glycol and neopentyl glycol. The NCL molecule contains a large number of benzene rings and unsaturated bonds, so the

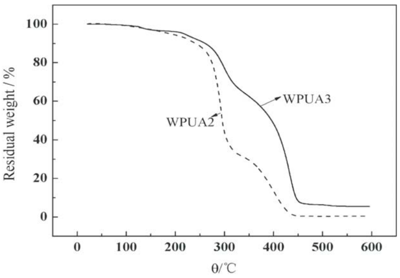

Figure 5. The TG curves of WPUA films with different kinds of poly diols.

Table 2. Decomposition temperature of WPUA films with different kinds of poly diols

Sample	$T_{0.05}$/°C	$T_{0.2}$/°C	$T_{0.3}$/°C	$T_{0.5}$/°C
WPUA2	190.00	274.00	284.00	295.00
WPUA3	217.65	294.24	316.14	395.86

Note: $T_{0.05}$, $T_{0.2}$, $T_{0.3}$, $T_{0.5}$ respectively for the corresponding temperature when the film weight loss rate of 5%, 20%, 30%, 50%.

rigidity of NCL increases. The better the rigidity of the molecule, the better its heat resistance [11]. And when the relative molecular mass of the soft segment is large, its crystallinity is better, and the degree of microphase separation of the soft and hard segments can be improved, and the thermal stability of WPUA can be improved [12].

5.2 Thermal Stability of WPUA Films with Different Kinds of Isocyanates

Thermal stability of the WPU films with different kinds of isocyanates were shown in Figure 6. It was found from Figure 6 that the thermal resistance of WPUA4 film is better than that of WPUA3 film. The thermal stability of WPUA4 film synthesized by HMDI was better than that of WPUA3 film synthesized by IPDI. Decomposition temperature of WPUA films with different kinds of isocyanates were shown in Table 3. The results showed that the decomposition temperature of WPUA4 film was higher than that of WPUA3 film by 13.84 °C, 10.00 °C, 11.70 °C, when the mass loss rate is 20%, 30%, 50%. In general, the thermal stability of the polymer elastomer is proportional to the rigidity, regularity and symmetry of the monomer [13,14]. The symmetry of HMDI molecule is better than that of IPDI, and the content of its rigid group will be higher. Therefore, using HMDI as raw materials can effectively improve the thermal stability of WPUA film.

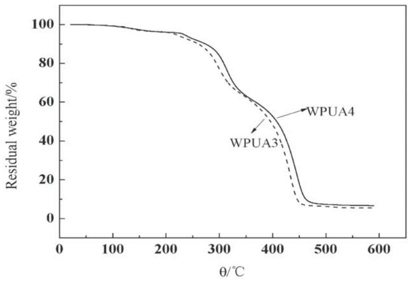

Figure 6. The TG curves of WPUA films with different kinds of isocyanates.

Table 3. Decomposition temperature of WPUA films with different kinds of isocyanates

Sample	$T_{0.05}$/°C	$T_{0.2}$/°C	$T_{0.3}$/°C	$T_{0.5}$/°C
WPUA3	217.65	294.24	316.14	395.86
WPUA4	232.82	308.08	326.14	407.56

Note: $T_{0.05}$, $T_{0.2}$, $T_{0.3}$, $T_{0.5}$ respectively for the corresponding temperature when the film weight loss rate of 5%, 20%, 30%, 50%.

5.3 Thermal Stability of WPUA Films with Different Kinds of Chain Extenders

Thermal stability of the WPU films was with different kinds of chain extenders were shown in Figure 7. And decomposition temperature of WPUA films with different kinds of chain extenders were shown in Table 4. It was found from Figure 7 that the thermal stability of WPUA5 film with using HQEE as chain extender was better than that of WPUA4 film with BDO as chain extender. The decomposition temperature of WPUA5 film was higher than that of WPUA4 film by 26.88 °C, 27.23 °C, 27.14 °C, when the mass loss rate is 20%, 30%, 50%. Compared HQEE with BDO, because of there has benzene ring structure in the HQEE molecule, using HQEE as chain extender increased the rigidity of the hard segment, and the thermal stability of WPUA5 was improved.

5.4 DSC Analysis of WPUA Films

The glass transition temperature (Tg) has been extensively studied in many polymers since it is one of the most fundamental features and is directly related to the properties of polymers. The changes in Tg for the WPUA modified by different kinds of isocyanates, polyalcohol and chain extender were presented in Figure 8. It was observed that all polyurethanes showed two glass transition

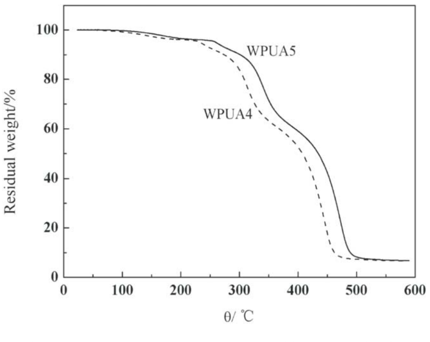

Figure 7. The TG curves of WPUA films with different kinds of chain extenders.

Table 4. Decomposition temperature of WPUA films with different kinds of chain extenders

Sample	$T_{0.05}$/°C	$T_{0.2}$/°C	$T_{0.3}$/°C	$T_{0.5}$/°C
WPUA4	232.84	308.08	326.14	407.56
WPUA5	257.90	334.96	353.37	434.70

Note: $T_{0.05}$, $T_{0.2}$, $T_{0.3}$, $T_{0.5}$ respectively for the corresponding temperature when the film weight loss rate of 5%, 20%, 30%, 50%.

temperatures due to the soft segment (Tg_s) and hard segments (Tg_h), the mainly reason is that the polyurethane soft segment and the hard segment produce a certain degree of micro-phase separation [15]. As is shown in Figure 8, the Tgs and Tgh both move to the high temperature direction with the increase of the rigidity and symmetry of the raw material molecules. And it is clearly seen that the Tg of WPUA5 was the highest, because of WPUA5 film was synthesized by NCL, HMDI and novel chain extender hydroquinone bis(β-ethyl) ether (HQEE), and the content of hard segments increased in the WPUA5 molecular chain, the rigidity of the WPUA5 increased. Therefore, the segments movement of the polyurethane was restricted, which maybe affect the mixing of the soft and hard segments in WPUA5 molecular chain, the micro-phase separation of the polyurethane was more favorable, and making Tg move to the high temperature direction.

5.5 The Analysis of WPUA Coatings

The properties of WPUA coatings modified by different raw materials were shown in Table 5. It was found from Table 5 that adding ethanol to the WPUA emulsion synthesized in this paper, the stability of the emulsion was unchanged, which indicated that the ethanol resistance of the emulsion was excellent. The heat resistance of WPUA film becomes better with the increase of the heat resistance of the film, because the emulsion synthesized in this experiment from WPUA2 to WPUA5, the better the rigidity, regularity and symmetry, the better the heat resistance. This article in the process of WPUA synthesis without adding volatile organic solvents, sodium hydroxide is used as neutralizer instead of triethylamine, which is a truly friendly environmental material with non-toxic, non-triethylamine, zero VOC, at the same time, it also meet the requirements of the tobacco industry package, so the experimental synthesis of the product can be considered as a coating used in the field of cigarette package.

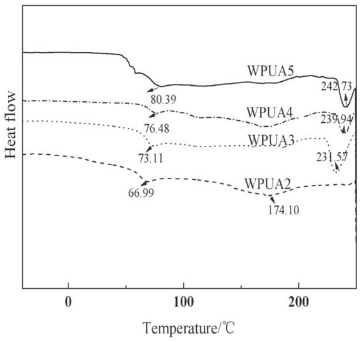

Figure 8. The DSC curves of WPUA films modified by different kinds of raw material.

Table 5. Properties of WPUA coatings

Sample	Ethanol resistance	Gloss testing (60°) ≥	Adhesion	Heat resistance
WPUA2	Stable	85	1	Changing
WPUA3	Stable	85	1	No change
WPUA4	Stable	85	1	No change
WPUA5	Stable	85	1	No change

6. Conclusions

The present study reported a high-temperature waterborne polyurethane-acrylate (WPUA) composite emulsion with a core-shell structure, zero VOC and without neutralizing agent triethylamine. The effects of different kinds of isocyanates, polyalcohol and chain extender on thermal stability of the WPUA films were investigated. The results showed that the decomposition temperature of WPUA film synthesized by NCL was higher than that of PCL by 100.86 °C when the mass loss rate is 50%. The decomposition temperature of WPUA film synthesized by HMDI was higher than that of IPDI by 11.70 °C when the mass loss rate is 50%. The decomposition temperature of WPUA film with using HQEE as chain extender was higher than that of WPUA film with BDO as chain extender by 27.14 °C when the mass loss rate is 50%. And Tg of polyurethane increased with the enhancement of the symmetry and rigidity of molecules.

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