

Synthesis and properties of UV/moisture dual curable polyurethane coatings

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Abstract:

UV curing technology is one technology with advantages such as environmental-friendly, efficiency, economy and energy saving. Due to even strict environmental protection policy, this new technology has gained a very rapidly development in the past few years and therefore being widely used in electronic packaging, surface protection of plastic device, flooring and small pitch car refinish. But it is restricted in the complicated shapes. In order to solve the problems, hyperbranched polyurethane was synthesized by "A₂+CB₂" one step way. A series of hyperbranched dual curable polyurethane resins based on modifying it had been synthesized. The results indicate that the coatings presented uniform mixing at microscopic level with phase continuity instead of forming the nanoparticle, which is because of the hydrolysis and condensation of alkoxy silanes. The researches on the surface topographies, dynamic mechanical properties, thermal properties and fundamental properties of the dual curable coatings indicated that the quality of the coatings enlarged firstly and then dropped with the increase of inorganic component; hyperbranched coatings have a good damping property and the thermal properties and fundamental properties of the dual curable coatings improve with the increasing of inorganic component.

Keywords: hyperbranched polyurethane; dual curable; organic-inorganic hybrid.

1. Introduction

UV-curable coating applications have gained wide interests, due to their advantages such as lower energy consumption, less environmental pollution, lower process costs, high chemical stability and very rapid curing even at ambient temperatures [1, 2]. UV-curable coatings are continually being developed by many leading suppliers in an effort to reduce any detrimental effects to the environment and to meet high standards required by industry. Especially, in the field of UV curing industries, urethane and acrylic urethane derivatives have been widely used in a variety of applications due to their versatility, durability, appearance and superior weatherability compared to other resin systems [3]. UV-curable coatings are widely used for protective purposes. For this reason, often the requirements ask for enhanced hardness, and superior thermal stability. Extensive researches have been made to obtain coatings that combine the desirable properties of organic polymers (elasticity, processability) and inorganic solids (hardness, chemical inertness and thermal resistance). Organic-inorganic hybrid coatings offer the opportunity to combine both these properties [4]. Recently, combining silica groups into urethane backbone for the formation of dual hybrid systems became an attractive way to significantly improve the mechanical and thermal properties of the resins [5-8].

Hyperbranched polymers are highly branched macromolecules and contain a large number of end-groups. Because of that they exhibit properties significantly different from those of their linear homologues (i.e. same nature and molar mass). They have high solubility and low viscosity compared to linear homologues. Except for the nature and structure of the backbone, their properties are to a large extent dependent

on the number and nature of their terminal groups and they can be modified by chemical modification of terminal groups. That leads to the possibility of designing the macromolecule with desired properties for any particular application [9].

The use of hyperbranched polymer in UV-curable application has been described in several papers [10-14]. The hyperbranched polymer has lower viscosity than conventional polyester urethanes of similar molecular weight. They exhibit very rapid cure rate and low shrinkage than conventional polyester urethanes. However, little work has been performed to prepare hyperbranched polymer for dual curable systems.

In this work, we prepared a series of hyperbranched dual curable polyurethanes (HDPUs) and the resins were used as oligomers to prepare dual curable coatings. The coatings were characterized from the aspects of morphologies, coating properties, dynamic mechanical properties and thermal properties.

2. Experimental

2.1. Material

2-Hydroxyethyl acrylate (HEA) supplied by Eternal Chemical Co. Taiwan, China, and was distilled under reduced pressure before use. Diethanolamine (DEOA), N, N-dimethylacetamide (DMA) are purchased from the First Reagent Co. Shanghai, China, and purified by reduced pressure distillation before use. Toluene-2,4-diisocyanate (TDI), butanedioic anhydride, N, N-dimethylaniline and dibutyl tin dilaurate (DBTDL) are purchased from the First Reagent Co. Shanghai, China, and used without further purification.

3-Glycidoxypropyltrimethoxysilane (KH560) was purchased from Nanjing Yudeheng Co., China. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) supplied by Ciba-Geigy, Switzerland.

2.2. Synthesis

2.2.1. Hyperbranched polyurethane (HPU)

The synthesis of hyperbranched polyurethane is straightforward as shown in Fig.

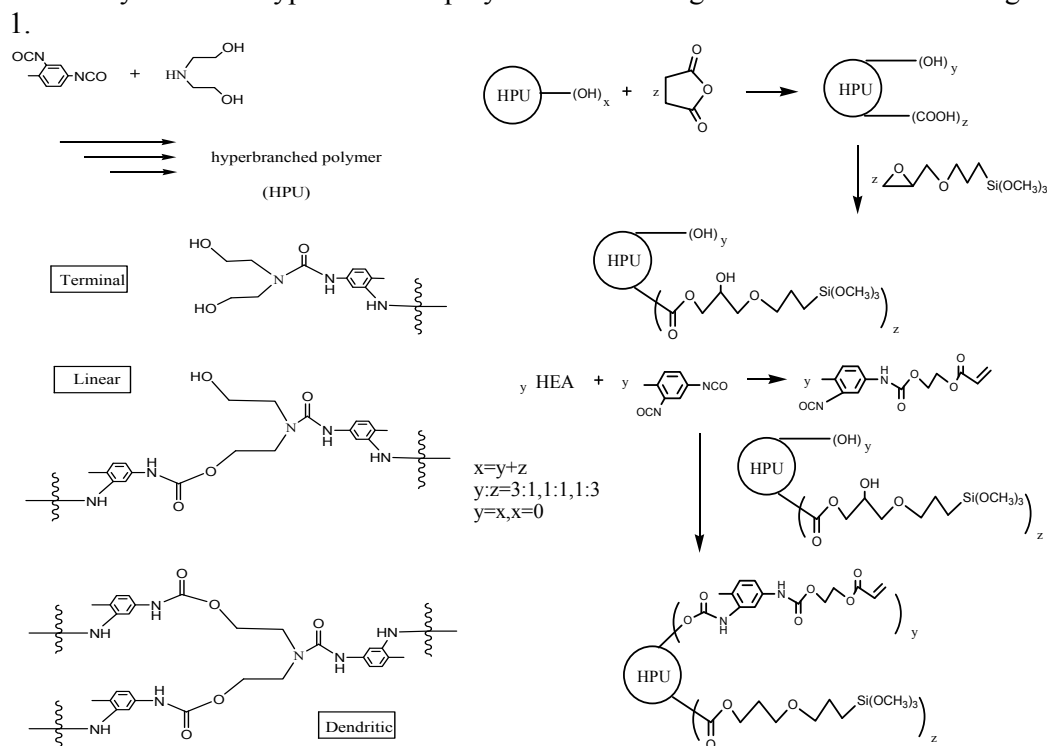


Fig.1 Outline of preparation process for HPU and HDPUs.

DEOA (12.6 g 0.12 mol) was dissolved in DMA (40 g) in a 250ml three-necked flask placed in an ice-water bath with a magnetic stirrer, a drop funnel and a N₂ inlet. The solution of TDI (17.4 g, 0.1 mol), DBTDL (0.2 g) and DMA (60 g) was then dropped slowly into the flask. The mixture was kept at 0-10 °C for 5 h. Then the flask was moved to an oil bath with a magnetic stirrer. The heating temperature of the reaction mixture was kept at 60 °C. The mixture was left to react until the value of isocyanate reached to the theoretical by titration, and then poured into toluene. The precipitate was collected and dried under vacuum, a yellowish viscous liquid was obtained, named HPU.

2.2.2. Hyperbranched dual curable polyurethane (HDPU)

The synthesis of hyperbranched dual curable polyurethane is straightforward as shown in Fig. 1.

The hyperbranched dual curable polyurethane was synthesized via a three-step procedure. The solution of HPU (7.5 g, -OH 0.04 mol by titration) and DMA (30 g) was poured in a 250 ml three-necked flask placed in an oil bath with a magnetic stirrer, a drop funnel and a N₂ inlet. Then butanedioic anhydride (2 g, 0.02 mol) was added into the flask. The heating temperature of the reaction mixture was kept at 80 °C for 12 h. KH560 (4.72 g, 0.02 mol) and N,N-dimethylaniline (0.1 g) was dissolved in DMA (15 g) and then poured into the above mixture and reacted in 80 °C until the value of acid group reached to the theoretical by titration.

Then, urethane monoacrylate (TDI-HEA) was obtained by the reaction of TDI (3.48 g, 0.02 mol) and HEA (2.32 g, 0.02 mol) in an equal mole dissolved in DMA (15 g) and stirred at 40 °C in the presence of DBTDL as a catalyst until the value of isocyanate reached to the theoretical one of mono-isocyanate by titration. Finally, the solution of TDI-HEA was poured into the above mixture and reacted in 60 °C until the value of isocyanate reached to the theoretical by titration, and then poured into toluene. The precipitate was collected and dried under vacuum, a yellow viscous liquid was obtained, named HDPU-1-1. HDPU-1-3 and HDPU-3-1 were synthesized by similar procedures as mentioned in synthesizing HDPU-1-1.

2.2.3. UV-curable Hyperbranched polyurethane (UV-HPU)

Similar procedures as mentioned in synthesizing HDPU-1-1 were used for synthesizing UV-HPU. The solution of TDI-HEA was poured into the solution of HPU and reacted at 60 °C until the value of isocyanate reached to the theoretical by titration, and then poured into toluene. The precipitate was collected and dried under vacuum, a yellowish viscous liquid was obtained, named UV-HPU.

2.2.4. Film preparation and UV curing

An appropriate amount of HDPU or UV-HPU was blended with 20 wt.% HEA as a monomer and 5 wt.% Darocur 1173 as a photoinitiator at room temperature for about 15 min until the solution became homogeneous. The transparent viscous formulations were cast onto glass plates by an applicator with 100- μ m gap. The coatings were exposed to a medium pressure Hg lamp (1kw, 20w/cm, made by lantian Co., China) for 1 min. After UV curing was successfully achieved, coated panels were immersed in distilled water at 40 °C and remained for 2 h to facilitate the hydrolysis.

Then the panels were annealed at 60 °C for 12 h and then stored at room temperature for 2 days. Via annealing, post-curing of alkoxy silane groups were performed.

The specimens used for DMA and SEM were prepared in an glass mold with the size of 10×10×2 mm and the two sides were irradiated using the same Hg lamp for 2 min.

2.3. Measurements

2.3.1. FTIR and ¹H NMR

The Fourier-Transformed infrared (FTIR) spectra were performed on a Bruker Vertex-70. The nuclear magnetic resonance (¹H NMR) spectrum was performed on an AVANCE AV 400 instrument (Bruker Co., Switzerland) using DMSO-d₆ as solvent.

2.3.2. The coating properties

The coating properties were measured in accordance with the corresponding standard test methods as indicated. This includes pendulum hardness (GB/T1730), pencil hardness (GB/T6739), gloss (GB/T9754), tape adhesion (GB/T9286).

2.3.3. SEM

Scanning electron microscopy (SEM) was performed on a QUANTA-200 scanning microscope to investigate the fracture surface of the hybrid materials.

2.3.4. Dynamic mechanical analysis

A DMA Q800 instrument (TA Co., USA) was run in a shear mode at an oscillation frequency of 50 Hz with a oscillation amplitude of 10.0 μm (~0.05% strain). The samples of around 10×10×2 mm were measured over a temperature range from -60 to 100 °C at a heating rate of 3 °C/min under nitrogen gas purging. The T_g^{DMA} values were taken from the peaks of tan δ curves.

2.3.5. Thermal properties

Thermal gravimetric analysis (TGA) was carried out on a Diamond TG/DTA PerkinElmer instruments using a heating rate 10 °C/min in nitrogen atmosphere from room temperature to 800 °C.

3. Results and discussion

3.1. Preparation and characterization

The four urethane resins based on partially modified hyperbranched polyurethane were synthesized. The hyperbranched polyurethane of the second and the third generation were synthesized from TDI (A₂) and DEOA (CB₂) via a one-step synthesis by a procedure described elsewhere [15].

The FTIR spectra of UV-HPU and HDPU-1-1 are shown in Fig. 2. The ¹H NMR spectra of HDPU-1-1 is shown Fig. 3. The disappearance of the characteristic absorption band at 2275 cm⁻¹ assigned to the isocyanate group of TDI and 2538 cm⁻¹ assigned to the acid group indicated the completion of the action in two cases. It also shows the characteristic N-H stretching band at 3310 cm⁻¹, carbonyl stretching band at 1720 cm⁻¹ and acrylic double bonds (C=C) at 810 cm⁻¹. The peaks at 1083 cm⁻¹ is the Si-O-CH₃ group of HDPU-1-1

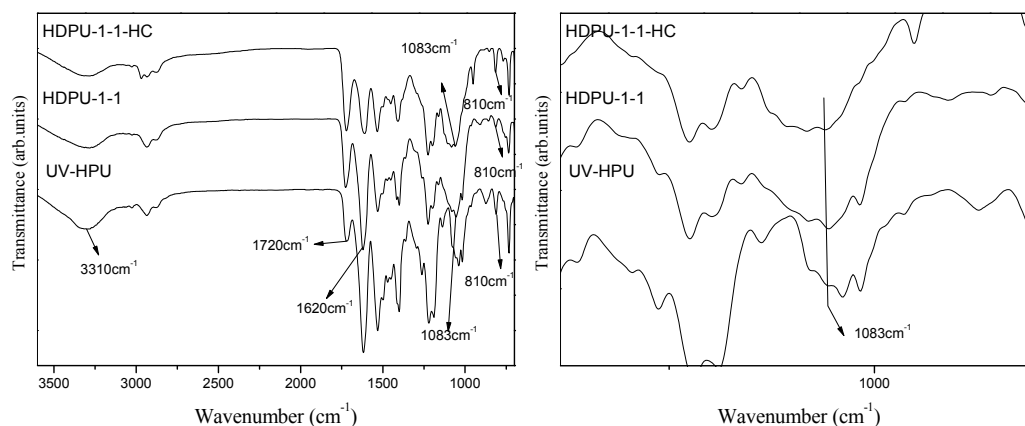


Fig. 2. FTIR spectrum of UV-HPU, HDPU-1-1 and HDPU-1-1-HC.

The typical FTIR spectra of the unannealed and annealed films of HDPU-1-1 are illustrated in Fig. 4. The peak at 810 cm^{-1} is separated from the other peaks, it is used to quantify the conversion of C=C bonds in UV-curable coatings, with the peak at 1720 cm^{-1} being due to C=O stretching absorbance as the reference for its invariability during UV curing. The intensity of the peak at 810 cm^{-1} for out-of-plane bending of C-H in C=C decreases with increasing exposure time under UV irradiation. The conversion of C=C bonds can be calculated according to the following equation:

$$\text{Conversion (\%)} = 100 \times (1 - A_t S_0 / A_0 S_t) \quad (1)$$

Where A_t and A_0 are the areas of the peak at 810 cm^{-1} and S_t and S_0 are the areas of the peak at 1720 cm^{-1} at an irradiation time t and $t=0$, respectively. Based on the data calculated by Eq. (1), the conversion of the unannealed and annealed films of HDPU-1-1 are 63.2 % and 78.3 %, respectively. The high conversion of C=C bonds is possibly attributable to the annealed process, which leads to post-curing of residual C=C bonds. The peak at 1083 cm^{-1} of Si-O-CH₃ group of the unannealed films of HDPU-1-1 can prove the possibility of moisture curing, while the disappearance of the peak at 1083 cm^{-1} of Si-O-CH₃ of the annealed films of HDPU-1-1 indicates the complete hydrolysis and condensation of trimethoxysilane.

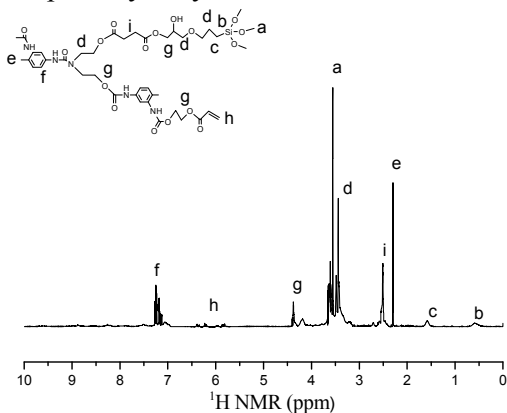


Fig. 3. ¹H NMR spectrum of HDPU-1-1.

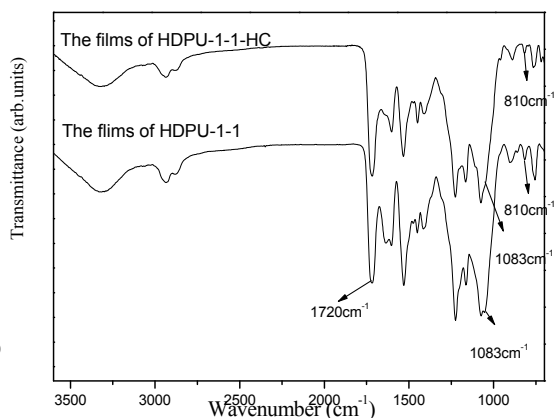


Fig. 4. FTIR spectrum of the films of HDPU-1-1 and HDPU-1-1-HC.

3.2 The coating properties

Various physical and mechanical characteristics of UV-HPU and HDPU coatings before and after annealing are given in Table 1. The hardness of the coating is the most important property affecting the abrasion and scratch resistance. Hard coatings give better scratch resistance, whereas abrasion resistance is also affected by surface friction. Chain flexibility and cross-linking density of network play a major role in the value of hardness. The pendulum hardness of before annealed coatings is UV-HPU > HDPU-3-1 > HDPU-1-1 > HDPU-1-3, whereas it changes to reverse after annealing. As to the pencil hardness, it takes place a great change after annealing. The pencil hardness of UV-HPU, HDPU-3-1, HDPU-1-1 and HDPU-1-3 changes from HB to 2H, from 6B to 3H, from 6B to 3H, from 6B to 4H. The great changes in the hardness can be attributed to alkoxy silane group's completely hydrolysis and condensation increasing the cross-linking density. It is also proved in the FTIR of the coatings and the DMA curves.

Coating's gloss is a complex phenomenon resulting from the interacting between light and the surface of the coatings. The influence of post-curing on gloss can be seen,

but the extent of the change is not obvious. The small increased gloss may be due to the post-curing of alkoxy silane group which resulted in more uniform film surface.

The adhesion of the coating is the most important property and indicates the capability of the resin combined with the floor. The influence of post-curing on adhesion can be clearly seen. UV-HPU coatings are not affected by annealing. After annealing, the adhesion of HDPU-3-1, HDPU-1-1 and HDPU-1-3 coatings shifts from 2 to 0. The increased adhesion may be due to the post-curing of alkoxy silane group which formed the Si-O-Si configuration with the glass plates and increased the reaction of the resin and the floor.

Table 1 Physical and mechanical of coatings on glass panels.

Sample	Post-cure (h)	Pendulum hardness	Adhesion (degree)	gloss		Pencil hardness
				20°	60°	
UV-HPU	0	120	2	170	162	HB
	12	128	2	170	162	2H
HDPU-3-1	0	78	2	187	172	6B
	12	212	0	192	180	3H
HDPU-1-1	0	72	2	188	174	6B
	12	238	0	194	182	3H
HDPU-1-3	0	68	2	187	170	6B
	12	256	0	195	184	4H

3.3. Morphologies

The SEM photographs of fracture surface of the material of HDPU-3-1, HDPU-1-1 and HDPU-1-3 are shown in Fig. 5. The SEM images show that it does not form the large nanoparticle and presents uniform mixing at microscopic level with phase continuity. It also indicates the hydrolysis and condensation of trimethoxysilane formed the organic Si-O-Si network structure.

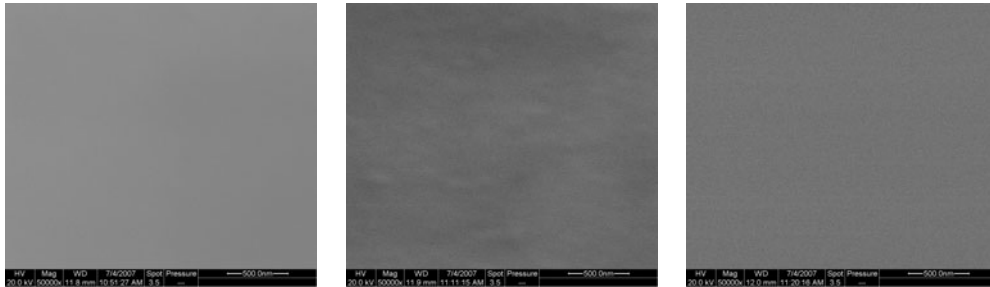


Fig. 5. SEM photographs of the fracture surface of the material of HDPU-3-1-HC, HDPU-1-1-HC and HDPU-1-3-HC.

3.4. Dynamic mechanical behaviors

When subjected to a sinusoidal dynamic stress, a polymeric beam in clamps will exhibit a sinusoidal tension that lags behind the applied stress with a phase angle δ . From the relation between stress and strain, the storage modulus E' and the loss modulus E'' can be calculated. The ratio of E''/E' is the loss tangent $\tan \delta$, which reflects the viscous-elastic characteristic of a polymeric material. The T_g^{DMA} values of polymeric material are obtained from the peaks of $\tan \delta$ curves [16].

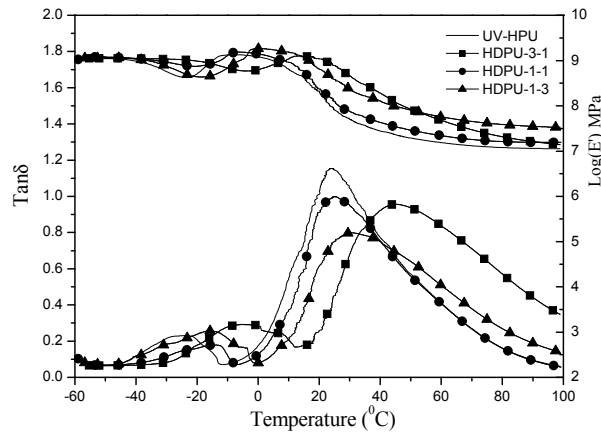


Fig. 6. DMA curves of UV-HPU, HDPU-3-1, HDPU-1-1 and HDPU-1-3 material.

The dynamic storage modulus (E') and $\tan \delta$ as a function of temperature for the material are shown in Fig. 6. We can see one important second-order transition appears besides T_g^{DMA} in $\tan \delta$ curves. It results from the side-chain motion that may be HEA used by our works. The T_g^{DMA} values of polymeric material are 24, 44, 25 and 30 °C for UV-HPU, HDPU-3-1, HDPU-1-1 and HDPU-1-3, respectively. With the increased alkoxy silane end group proportion of the resin, the cross-link density of the material increase. The hydrolysis and condensation of trimethoxysilane formed the organic Si-O-Si network structure. The organic Si-O-Si chain is a softening chain and increases the chain motion flexibility. The two factors, the cross-link density of the material and the chain motion flexibility, maybe play the important roles in the dynamic mechanical behaviors. The DMA curves may be the result of the increased cross-link density reacts with the increased chain motion flexibility. Then it is easy to explain that the T_g^{DMA} values of polymeric material are HDPU-3-1>HDPU-1-3>HDPU1-1 \approx UV-HPU. As for HDPU-3-1 material, the increased cross-linking density played the decisive part in the dynamic mechanical behaviors. As to HDPU-1-1 material, the increased cross-linking density balances with the increased chain motion flexibility. It is why that the DMA curve of HDPU-1-1 was similar with the DMA curve of UV-HPU. As for HDPU-1-3 material, it had a higher the cross-link density than the other materials. The increased chain motion flexibility did not completely counteract the increased cross-linking density. As can be seen in Fig. 6, the peak value of $\tan \delta$ is 1.15, 0.91, 0.99 and 0.79 for UV-HPU, HDPU-3-1-HC, HDPU-1-1-HC and HDPU-1-3-HC, respectively. The factors affected to the $\tan \delta$ value is very complex. However the high $\tan \delta$ value of hyperbranched polymer makes them a good candidate for damping material.

3.5. Thermal properties

Nanocomposites in many systems have shown higher thermal stability than pure organic polymer due to the strong interaction between organic and inorganic components. The TGA and DTG curves of UV-HPU, HDPU-3-1, HDPU-1-1 and HDPU-1-3 films are shown in Fig. 7. The TGA results of the films are listed in Table 2. It can be seen that the condensed inorganic linkage in HDPUs have obvious effect in improving the thermal stability of the coatings. All samples show a small weight loss around 100 °C implying the release of volatile degradation products such as unreacted photoinitiator and reactive diluent. One can see that the sample of HDPU-1-3 exhibited a 10 % weight loss at around 255 °C higher than other samples.

It is clearly observed that the thermal stability of HDPU network is improved compared with UV-HPU network. Thermogravimetric analyses shows that (Table 2) with increasing the alkoxy silane groups, the delaying of degradation temperatures shifts to higher values. The delay in degradation caused by the siloxane moiety may be attributed to the steadiness of inorganic structure, which may stabilize the polyurethane resin. The first stage decomposition process is the main degradation of urethane, and the second stage decomposition process is the main degradation of C-C main-chain. More inorganic Si-O-Si linkages in HDPU greatly inhibited the heat diffusion, and thus postponed the decomposition of organic parts. The delaying of starting degradation temperatures in the first stage is much larger than that in the second stage, indicating that the protection of organic part by inorganic network is more distinct for the organic part which is more close to the inorganic networks.

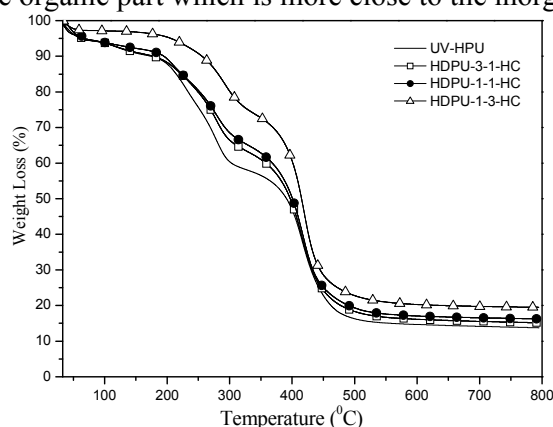


Fig.7. The TGA and DTG curves of UV-HPU, HDPU-3-1, HDPU-1-1 and HDPU-1-3 films
 Table 2 Thermal properties of UV-HPU, HDPU-3-1-HC, HDPU-1-1-HC and HDPU-1-3-HC films

Sample	Temperature of weight loss (°C)				Residue at 800 °C (%)
	10 %	30 %	40 %	50 %	
UV-HPU	172	268	302	390	13.77
HDPU-3-1-HC	177	284	357	396	15.17
HDPU-1-1-HC	194	292	367	400	16.25
HDPU-1-3-HC	255	370	401	414	19.52

4. Conclusion

In this paper a series of hyperbranched dual curable polyurethane resins were prepared based on the chemical modification of hyperbranched polyurethane and were characterized by FTIR and ¹H NMR. The polymers were used as oligomers in dual curable compositions. Upon increased inorganic content, the dual curable coating properties such as pendulum hardness, pencil hardness, gloss and adhesion are improved.

The dual curable materials were also characterized by SEM, DMA and TGA. It was found that it did not form the large nanoparticle via the hydrolysis and condensation reaction and presented uniform mixing at microscopic level with phase continuity. By the comparison of the property of the four series of materials, it was found that the thermal stability property was improved great upon increasing inorganic content. From the DMA data, one important second-order transition appeared, it resulted from the side-chain motion that may be HEA used by our works. The T_g^{DMA} values of polymeric material was HDPU-3-1>HDPU-1-3>HDPU1-1≈UV-HPU. It may be the result of the increased cross-link density reacted with the increased chain motion flexibility. In a word, the

hyperbranched dual curable polyurethane is promising as oligomers for UV curable coatings, ink, adhesives and damping material.

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