Fluorinated Hyperbranched Polyurethane Acrylates used as additives for UV Curing Systems

Hui Miao, Liangliang Cheng, Wenfang Shi/ Department of Polymer Science and Engineering, University of Science and Technology of China/ Hefei, Anhui, 230026, P. R. China

Abstract

The fluorinated hyperbranched polyurethane acrylates (FHUAs) were synthesized by modifying the hyperbranched polyester Boltorn H20 with fluorinated isocyanate, and characterized with ^{1}H NMR and FTIR spectra. The thermal behavior of FHUAs was monitored by TGA. The water and oil wettability of UV-cured polyurethane films with FHUAs introduced as additives were investigated by measuring the contact angles. The results showed that an extremely low concentration of FHUAs, even below 0.1 wt %, will efficiently decrease the surface tension of UV-cured film to 10-15 mN/m and make the films highly hydrophobic and oleophobic. The obtained film with the addition of FHUA 1 is stable in acidic and neutral solutions and still has good water repellency after immerging in the solution of pH 1 for couple days. The X-ray photoelectron spectroscopy analysis confirmed the increase of surface densities of perfluoroalkyl groups, and showed that the molecule with the highest ratio of perfluoroalkyl groups has the best ability of assembling at the surface of the UV-cured film.

Key words: water and oil repellence; perfluoroalkyl; UV-curing;

1. Introduction

Fluorinated polymers have special properties because of their low surface energy. The polymers can be applied to various kinds of organic coatings, such as outdoor architectural coatings, protective coatings for large machines and transportations, and will endow the coating a surface with very low surface energy and wonderful hydrophobicity and oloephobicity [1-5]. In order to obtain a surface with low surface energy, only a very small quantity of fluorinated compound is needed, because of the self-stratification strategy [6].

Hyperbranched polymers are a kind of dendritic polymer, which has peculiar properties. They have densely hyperbranched structures and large number of endgroups, which provide themselves excellent flow and processing properties, especially a lower viscosity than their linear counterparts with comparable molecular weights [7], which makes them interesting for UV-curing systems [8-11]. The photopolymerization of multifunctional monomers makes it easy and efficient to generate a

three-dimensional polymeric network. We have described UV curable waterborne polyurethane based on hyperbranched aliphatic polyester[12,13] and hyperbranched polyphosphate acrylate used as UV curable flame retardant coatings[14].

The fluorinated hyperbranched polymers have been reported in literature[15-18]. W. Ming etc. obtained low surface energy films based on fluorinated isocyanates and modified hyperbranched polyesters, and concentrated on the temperature effects[15]. Marco Sangermano etc. synthesized a fluorine-containing hyperbranched polymer used as additive in cationic photopolymerizations[16].

In this work, fluorinated hyperbranched polyurethane acrylates (FHUAs) were synthesized by modified the hyperbranched polyester Boltorn[TM] H20 with fluorinated isocyanate, and characterized with ^{1}H NMR and FTIR spectra. The thermal behavior of FHUAs was monitored by TGA. The water and oil wettability of UV-cured polyurethane film with FHUAs introduced as additives were investigated by contact angles measurement. The stability of films with the addition of FHUA 1 in acidic and neutral solutions was discussed. The X-ray photoelectron spectroscopy analysis was used to reveal the assembling mechanism at the surface of film.

2. Results and discussion

Synthesis and characterization

As shown in Fig. 1, FHUA is an oligomer based on hyperbranched polyester (H20) as a core with fluorinated and acrylic terminal groups. By changing the value of m, different oligomers can be obtained. Here, m was 8, 4, and 2, corresponding to FHUA 1, FHUA 2, and FHUA 3, respectively.
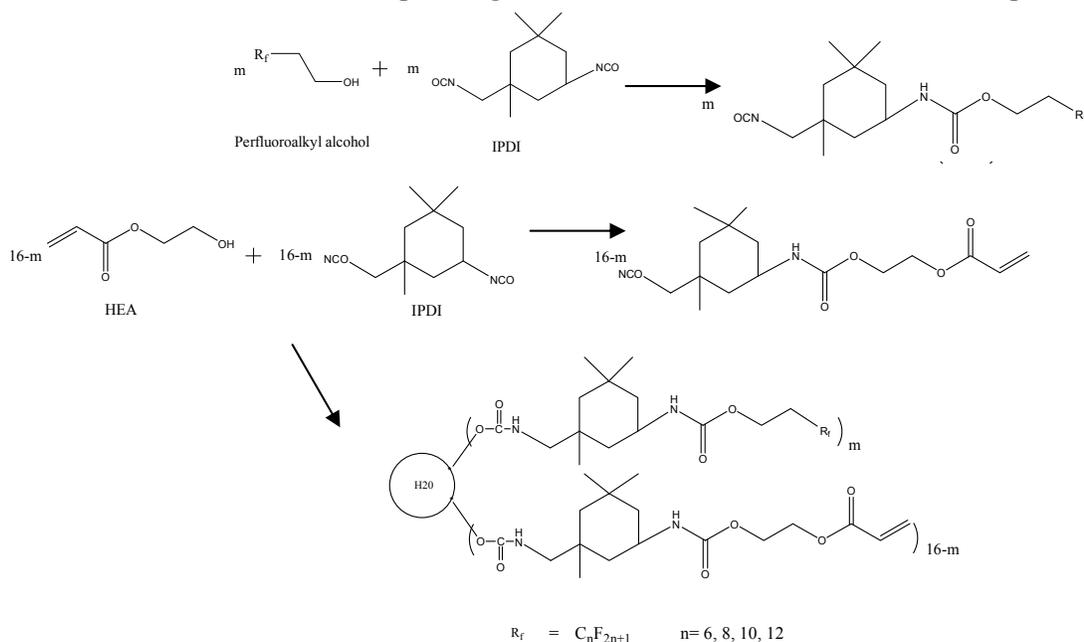
Fig. 1 Idealized formula of Boltorn H20, and schematic outline for the synthesis of HFUAs.

The FTIR spectra of FHUAs are given in Fig. 2. The peak at 3400 cm^{-1} and 1535 cm^{-1} is ascribed to N-H stretching vibration and N-H deformation vibration, respectively. The intensive absorption at 1240 cm^{-1} is ascribed to C-F stretching vibration. The strong absorption bands at 1641, 1411 and 810 cm^{-1} indicates the existence of acrylic groups.

The ^{1}H NMR spectra of FHUAs with the assignments are shown in Fig. 3. Three groups of characteristic peaks at 5.70-6.60 ppm are obviously observed, which prove the existence of acrylic group in FHUAs. The peaks at 4.00-4.49 ppm are assigned to the hydrogen atoms of the methylene connected to ester group. The peaks at 3.36-3.89 ppm are assigned to the hydrogen atoms of methylene connected to ether group or hydroxyl (the unreacted terminal groups of H20). The peaks at 2.75-3.06 ppm are assigned to hydrogen atoms of methylene or methyne connected to the amide group. The peaks at 2.30-2.61 ppm are observed, which are characteristic peaks of hydrogen atoms of the methylene connected to the perfluoroalkyl group. The peaks below 2.0 ppm are assigned to the methyl and methylene groups in the molecular structure. From the ^{1}H-NMR spectra, the molar ratio of the acrylic double bonds and perfluoroalkyl groups in the molecular structure can be calculated easily.

Through the FTIR and ^{1}H-NMR analysis, it can be confirmed that the reaction was carried out as our predicted outline, and the acrylic double bond groups and the perfluoroalkyl groups are both introduced.
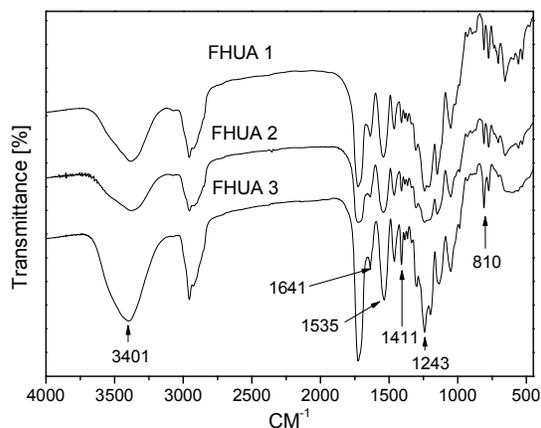
Fig. 2. FTIR spectra of FHUAs.
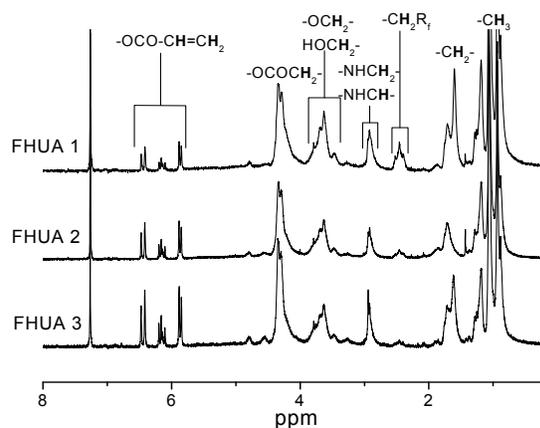
Fig. 3. ^{1}H NMR spectra of FHUAs.

Surface property of the cured films
Water and oil wettability

A series of samples were prepared by adding FHUAs into the EB270/HDDA (w/w=7/3) resin at the concentration ranging from 0.01 up to 1 wt%, and exposed to a Fusion UV lamp to obtain cured transparent films. When the concentration was raised to 1 wt%, FHUA 1 and FHUA 2 are not dissolved well in the acrylate resin, so the samples at this concentration of FHUA 1 and FHUA 2 are not measured.

The water and oil wettability of the cured film surface were measured by the contact angles of water and oil drops. 1-Bromonaphthalene was used as an oleophilic compound. The surface tension γ_s of cured FHUAs films was calculated from the contact angles by using Equation 1 and 2.

Equation 1: $\gamma_s = \gamma_s^d + \gamma_s^p$

Equation 2: $(1+\cos\theta)\gamma_l = 4\left(\dfrac{\gamma_l^p \gamma_s^p}{\gamma_l^p + \gamma_s^p} + \dfrac{\gamma_l^d \gamma_s^d}{\gamma_l^d + \gamma_s^d}\right)$

Table 1. Contact angles of water and 1-bromonaphthalene on UV-cured polyurethane (EB270/HDDA) films with different concentrations of FHUAs.

Concentration (wt. %)	Contact angle (^{o})	
	Water	1-Bromonaphthalene
FHUA 1		
0	88	38
0.01	105	66
0.05	121	94
0.1	119	93
0.5	118	93
FHUA 2		
0	88	38
0.01	100	46
0.05	108	74
0.1	113	84
0.5	112	87
FHUA 3		
0	88	38
0.01	97	42
0.05	99	47
0.1	102	58
0.5	110	85
1	109	84

Table 1 lists the water and oil contact angles on the UV-cured polyurethane (EB270/HDDA) films with different concentrations of FHUAs. It is clear that the water and oil wettability of the cured films depend on the concentration of FHUAs: the contact angle increases by adding more FHUAs. By adding FHUA 1, the films become highly hydrophobic with asymptotic dependence on the concentration, and the maximum values of the contact angles overcome 120°. For the oil test, the same trend can be observed. The UV-cured films become more oleophobic with an evident increase of contact angle from 38° to above 90°. For the other two FHUAs the similar results are obtained but lower maximum contact angle values (around 110° and 80° respectively).

Table 2. Surface tension of UV-cured films with different concentrations of FHUAs, and the surface tension parameter of the test liquids, water and 1-bromonaphthalene.

Sample		γ	γ^d	γ^p
water		72.8	21.8	51.0
1-Bromonaphthalene		44.4	44.4	0
FHUA 1				
	0	41.5	35.7	5.8
	0.01	26.2	23.9	2.3
	0.05	13.8	13.5	0.3
	0.1	14.7	13.8	0.8
	0.5	15.1	13.5	1.6
FHUA 2				
	0	41.5	35.7	5.8
	0.01	34.4	32.2	2.2
	0.05	22.2	20.4	1.8
	0.1	18.3	16.6	1.7
	0.5	18.0	15.6	2.5
FHUA 3				
	0	41.5	35.7	5.8
	0.01	37.0	34.1	2.9
	0.05	34.4	31.8	2.6
	0.1	29.4	27.1	2.3
	0.5	18.9	16.1	2.8
	1	19.7	16.8	2.9

The calculated surface tensions γ_s of cured FHUAs films are listed in Table 2. It can be observed that by adding extremely low concentration of FHUAs, the surface tension comes down sharply from 41.5 to 13.8 (the lowest value).

From Tables 1 and 2 it can be concluded that the concentration of FHUAs at which the film becomes highly hydrophobic (critical concentration) is always extremely low. FHUA 1 has the lowest critical concentration below 0.05 wt %, while FHUA 2 is about 0.1 wt % and FHUA 3 is about 0.5 wt %. Obviously, the more perfluoroalkyl groups the molecule structure has, the lower critical concentration it will exhibit. More importantly, FHUA 1 has farthest enhanced the water and oil contact angles and reduced the surface tensions, while the others can never achieve no matter how much were added into. This indicates that after the modification of H20, the molecule with more perfluoroalkyl groups is more effective in improving the water and oil repellence of the UV-cured films.

Chemical stability

The UV-cured film with addition of 0.1 wt % FHUA 1 was dunked into various pH aqueous solutions for couple days. Fig. 6 shows that UV-cured film with 0.1 wt% FHUA 1 are stable at acidic and neutral solutions during the period. When immerged with an alkali aqueous solution, the contact angles are diminished continuously, and especially for solution of pH 14, the values fall down sharply after immerging for couple hours. These results show that the additive FHUA 1 can endure acidic environmental conditions for a long time but can not withstand alkali conditions.
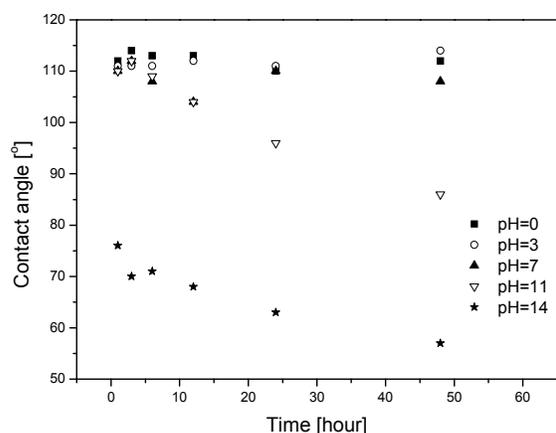
Fig. 4. Chemical stability of the cured films containing 0.1 wt% FHUA 1.
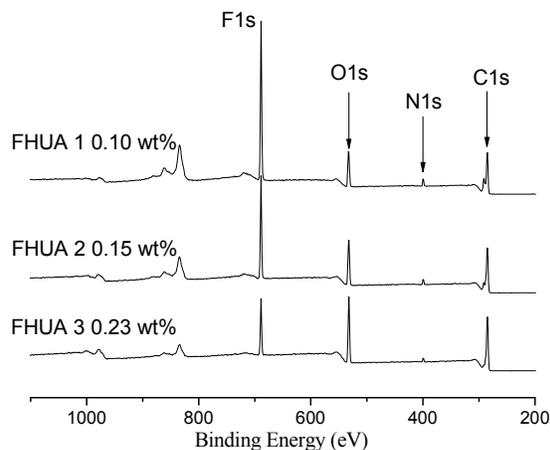
Fig. 5. XPS curves of polyurethane films with addition of FHUAs.

Surface composition of the cured film

In the contact angle measurement, the water and oil contact angles of the UV-cured films are enhanced with the addition of extremely low concentration of FHUAs, which indicates the assembly of low surface energy components (perfluoroalkyl groups) at the interface. Therefore, the fluorine concentration at the interface is much higher than the interior of film, which was proved by XPS analysis.

The XPS spectra of the region corresponding to 0-1100 eV for the films are presented in Fig. 5. From the survey scan, the signals of fluorine, oxygen, nitrogen and carbon can easily be observed, with bonding energies of 688, 532, 399 and 290 eV respectively. The high-resolution C1s XPS spectra of the film containing 0.1 wt % FHUA 1(Fig. 6) show four different binding energies. The peak between 284 and 290 eV arises from the overlap of three different kinds of carbon [C-C (284.6 eV), C-OH (286.1eV), O=C-OH (288.9 eV)]. The peaks at, 291.3 and 293.6 eV are assigned to the binding energy of CF_2 and CF_3, respectively.
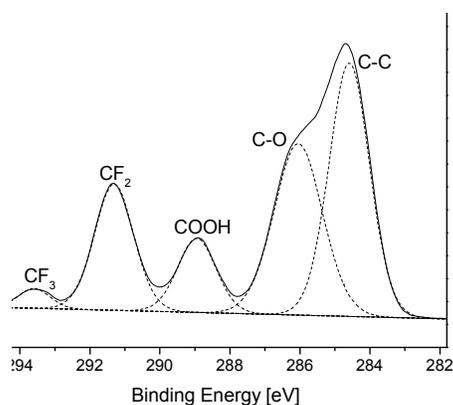
Fig. 6. High-resolution C1s XPS spectra
of film containing 0.1 wt % FHUA.
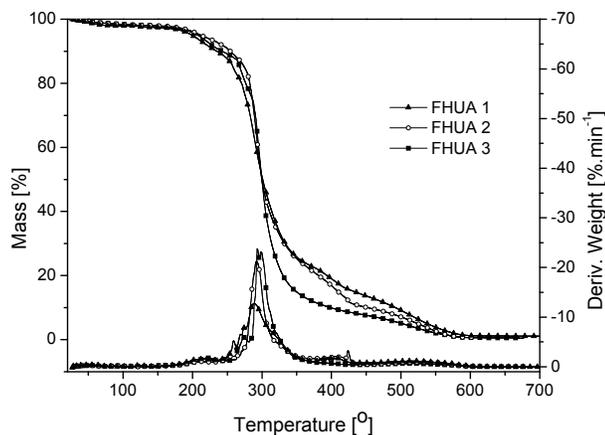
Fig. 7. TGA and DTG curves of the FHUAs.

As concerned, the fluorine content at the surface of the three samples calculated from the XPS measurement is listed in Table 3. In the UV-cured films, FHUA 1, FHUA 2 and FHUA 3 were introduced with concentration of 0.10, 0.15 and 0.23 wt % respectively. According to the molecule structure of FHUAs, the fluorine content of each formula can be calculated. Thus the fluorine content in the UV-cured films is obtained and listed in Table 3. In film bulk, the above three samples have the same fluorine content, 0.027 wt %, while at the interface the fluorine concentration is 43.1, 29.7 and 18.1 wt %, respectively, which proves the perfluoroalkyl groups assembly at the interface, and on the other hand, that the formula FHUA 1 is the most effective on migrating to the interface and thereby improving the water and oil repellence of the UV-cured films. For further comparison, sample 4 with 0.50 wt % concentration of FHUA 2 was measured. At this condition, the fluorine content in the film bulk is three times more than that of the sample 1, but at the interface, the value is 30.9 wt%, which is much lower than that of the sample1 and slightly high than that of the sample 2. It is indicated that when above the critical concentration, the fluorine content at the interface is independent on the concentration and lies on the molecule structure of the additives (FHUAs). Here, it can be said that the molecule which has more perfluoroalkyl groups is more effective on assembling at the interface of the UV-cured film, which is the same conclusion we obtained from the contact angle measurement.

Table 3. The fluorine content at the surface of the UV-cured films.

Sample	Concentration (wt %)	F content (wt %) in film bulk	F content (wt %) at the interface
1	FHUA 1 0.10	0.027	43.1
2	FHUA 2 0.15	0.027	29.7
3	FHUA 3 0.23	0.027	18.1
4	FHUA 2 0.50	0.090	30.9

Thermal properties

The thermal degradation behaviors of FHUAs were investigated by TGA at constant heating rate of 10 ^{o}C.min^{-1} in air, and the TGA and DTA curves are shown in Fig. 7. It can be seen that all samples show a thermal stability at 180 ^{o}C with a small weight loss of less than 3%. When raised to 200 ^{o}C the weight loss of all samples begins to increase. The largest peaks with loss of weight are observed in the range of 280-310 ^{o}C in all DTG curves. Moreover, it can be found another degradation stage between 400-450 ^{o}C for FHUA 1 and FHUA 2. This is because of the more content of the perfluoroalkyl group in the two molecules. The fluorine carbon bond is quite thermal stable due to its high bond energy. In the degradation process, the molecule fragment containing the perfluoroalkyl group needs high temperature to degrade completely. When raised to 580 ^{o}C, all the samples degrade almost completely.

3. Conclusion

The fluorinated hyperbranched polyurethane acrylates (FHUAs) were synthesized successfully by modifying the hyperbranched polyester Boltorn^{TM} H20 with fluorinated isocyanate. The contact angle results showed that an extremely low concentration of FHUAs, even below 0.1 wt %, will efficiently decrease the surface tension of UV-cured film and make the films highly hydrophobic and oleophobic. The obtained film with addition of FHUA 1 is stable in acidic and neutral solutions. The X-ray photoelectron spectroscopy analysis showed that the formula with the highest ratio of perfluoroalkyl groups has the best ability of assembling at the surface of the UV-cured film.

4. Experimental

4.1 Materials

Perfluoroalkyl alcohol was a mixture with its molecular general formula $C_nF_{2n+1}CH_2CH_2OH$ (n=6, 8, 10) and molecular weight 454.5, supplied by Shanghai Luoyin Fluoro. Chem. Co. China. The hyperbranched aliphatic polyester was supplied Perstorp AB, Perstorp, Sweden. The hyperbranched aliphatic polyester Boltorn H20 was supplied by Perstorp AB, Perstorp, Sweden. Isophorone diisocyanate (IPDI) was used after distillation. Di-n-butyltindilaurate (DBTDL) was used as a catalyst, and hydroquinone methylether was used as an inhibitor. N, N-dimethyl acetamide and 1, 4-dioxane were dried over potassium hydroxide and then distilled. All the chemicals for the synthesis were supplied by Shanghai First Reagent Co. China. 2-hydroxy-2-methyl-1-phenyl-1-propanone (Runtecure 1103), used as a photoinitiator, was supplied by Runtec Co., Changzhou, China. Hydroxyl ethyl acrylate, 1, 6-hexyldiol diacrylate, 1, 6-hexanedioldiacrylate and polyurethane acrylate (EB270) were supplied by Eternal Chemical Co., Taiwan.

4.2 Synthesis of FHUAs

The ideal molecular formula of Boltorn H20 and a schematic outline for the reaction procedure are shown in Fig.1. The molecular weight of Boltorn H20 is 1747 g mol^{-1} with polydispersity of 1.3 and an average of 16 hydroxyl end groups per molecule. In the first step, IPDI (4.45 g, 0.02 mol) diluted by DMAc (20 mL) was added in a three-necked, round-bottomed flask equipped with a mechanical stirrer,

dropping funnel, reflex condenser with a drying tube and N_2 protection. After dissolving 0.1 wt% DBTDL (catalyst), a solution of perfluoroalkyl alcohol (9.54 g, 0.021 mol) predissolved with DMAc (60 mL) was slowly dropped into the above reaction vessel, and left stirring at $50^{\circ}C$ for 12 h. Meanwhile, in another same reaction equipment, IPDI (4.45 g, 0.02 mol) diluted by DMAc (20 mL) and 0.1 wt% DBTDL were added, and a solution of HEA (2.43 g, 0.021 mol) diluted by DMAc (20 mL) was added dropwise into the reaction vessel, and left stirring at $50^{\circ}C$ for 12 h.

In the second step, H20 (4.37 g, 2.5 mmol) and DMAc (50 mL) were added into a three-necked, round-bottomed flask equipped with a mechanical stirrer, reflex condenser with a drying tube and N_2 protection. After the addition of 0.05 wt% hydroquinone methylether (inhibitor) and 0.1 wt% DBTDL, the two reaction mixture gotten from the first step were added in the reaction vessel. The reactant was left stirring at $90^{\circ}C$ for 24h.

After got back to the room temperature, the reaction mixture was poured into a large amount of distilled water, and a yellowish precipitate formed and was collected by filtrating. The obtained solid was redissolved in 1, 4-dioxane and was precipitated in water again. After filtration and drying in a vacuum oven, a product named FHUA 1 (m =8) was abtained. IR ($vmax\ cm^{-1}$): 3392, 2958, 1727, 1637, 1536, 1463, 1409, 1301, 1241, 1199, 1133, 1052, 808, 775. ^1H NMR δ ppm: 6.42 (dd, J_1=1.5 Hz, J_2=17.4 Hz), 6.11 (dd, J_1=10.5 Hz, J_2=17.4 Hz), 5.82 (dd, J_1=1.5 Hz, J_2=10.5 Hz), 4.48-3.96 (m), 3.94-3.37 (m), 3.03-2.76 (t), 2.58-2.33 (t, J=17.4 Hz), 1.82-1.46 (m), 1.34-0.59 (m).

With different molar ratios, while m was 4 and 2, the molecules FHUA 2 and FHUA 3 were obtained, respectively. All the products were white or yellowish solid and could be easily pestled into white powder, which could be applied to the formulation much easier during the dissolution process.

4.3 Sample preparation

The formulation containing FHUAs, HDDA, EB270, and 3 wt% Runtecure 1103 was applied on a glass slide with an applicator to obtain a thickness of about 100 μm, and then exposed to a medium pressure Hg lamp (300W in^{-1}, Fusion UV Systems, Inc. USA) in air to form the tack free film for the contact angle measurement and XPS analysis.

4.4 Measurements

The FTIR spectra were recorded with a MAGNA-IR 750 spectrometer (Nicolet Instrument Co., USA). The ^1H NMR analysis was performed on a DMX-500MHz apparatus (Brucker Co., Switzerland) using $CDCl_3$ as a solvent and TMS as a reference.

The contact angle measurements were performed with a JC2000A instrument at room temperature (20 $^{\circ}C$) with the sessile drop technique. At least eight measurements were performed on every sample, and the difference from the average value was no more than 8°.

The X-ray photoelectron spectroscopy (XPS) data were obtained using a physical electronics (PHI QUANTERA) XPS/ESCA system. The takeoff angle of the electron was 90° with respect to the surface of the sample.

The thermogravimetric analysis (TGA) was carried out on a Shimadzu TG-50 apparatus under an air atmosphere at purge rate of 80 mL min^{-1}. Heating rate was 10 ^{o}C min^{-1}. For each experiment approximately 10.0 mg sample was used in the TGA test.

Acknowledgment

Reference:

[1] R. Bongivanni, F. Montefusco, A. Priola, N. Macchioni, S. Lazzeri, L. Sozzi, B. Ameduri, Prog. Org. Coat. 45 (2002) 359-363.

[2] B. Ameduri, R. Bongivanni, V. Lomberdi, A. Pollicino, A. Priola, A. Recca, J. Polym. Sci. A Polym. Chem. 39 (2001) 4227-4235.

[3] L. van Ravenstein, W. Ming, R. D. van de Grampel, R. van der Linde, G. de With, T. Loontjens, P. C. Thüne, J. W. Niemantsverdriet, Macromolecules, 37 (2004) 408-413.

[4] M. Morita, H. Ogisu, M. Kubo, J. Appl. Polym. Sci. 73 (1999) 1741-1749.

[5] D. K. Kim, S. B. Lee, K. S. Doh, Y. W. Nam, J. Appl. Polym. Sci, 74 (1999) 2029-2038.

[6] W. Funke, Prog. Org. Coat. 2 (1973) 289-293.

[7] B. Voit, J. Polym. Sci., Part A: Polym. Chem. 38 (2000) 2505-2511.

[8] E. Džunuzović, S. Tasić, B. Božić, K. Jeremić, B. Dunjić, React. Funct. Polym. 66 (2006) 1097-1105.

[9] L. E. Schmidt, Y. Leterrier, D. Schmäh, J. E. Månson, D. James, E. Gustavsson, L. S. Svensson, J. Appl. Polym. Sci., 104 (2007) 2366-2376.

[10] S. Tasic, B. Bozic, B. Dunjic, Prog. Org. Coat. 51 (2004) 321-328.

[11] M. Sangermano, G. Malucelli, R. Bongiovanni, A. Priola, A.Harden, Polym. Int. 54 (2005) 917-921.

[12] A. Asif, W.F. Shi, C. Y. Huang, Colloid Polym. Sci. 283 (2004) 200-208.

[13] A. Asif, W.F. Shi, X. F. Shen, K. M. Nie, Polymer 46 (2005) 11066-11078.

[14] Z. G. Huang, W.F. Shi, Eur. Polym. J. 43 (2007) 1302-1312.

[15] W. Ming, F. Melis, R. D. van de Grampel, L. van Ravenstein, M. Tian, R. van der Linde, Prog. Org. Coat. 48 (2003) 316-321.

[16] M. Sangermano, A. Di Gianni, R. Bongiovanni, A. Priola, B. Voit, D. Pospiech, D. Appelhans, Macromol. Mater. Eng. 290 (2005) 721-725.

[17] J. J. Shao, X. H.Yang, Y. H. Liu, X. L. Wang, J. Appl. Polym. Sci. 98 (2005) 238-242.

[18] M. Li, X. H. Yang, Y. H. Liu, X. L. Wang, J. Appl. Polym. Sci. 101 (2006) 317-322.