

Synthesis of Waterborne Perfluoroacrylic Polyurethane Composite and Its Property

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The waterborne perfluoroacrylic polyurethane composite (WFPUC) series were prepared by the emulsion polymerization (WFPUC-E) and the physical blending (WFPUC-B). WFPUC-E was prepared by polymerizing perfluoroalkyl ethyl acrylate (FA) and waterborne polyurethane (WPU), and WFPUC-B was prepared by blending FA copolymer and WPU. The structures of the synthesized WFPUC were identified by using FT-IR-ATR. The surface and thermal properties of the synthesized WFPUC were investigated by measuring contact angle, surface energy, and TGA. The surface energy of WFPUC-E was lower than that of WFPUC-B. The thermal stability of the WFPUC-B showed better than that of the WFPUC-E.

Key Words : Waterborne fluoroacrylic polyurethane composite, Waterborne polyurethane

1. Introduction

Polyurethane has many useful features in the field of adhesives, coatings, foams, and various industrial materials. It has a number of different reactive groups so that its physical properties can be changed easily and exhibits the excellent physical properties such as high tensile strength, abrasive resistance, flexibility, and processability^{1,2)}. Generally polyurethane has other functional groups including ester, ether, urea and amide together with bond such as $[-NH-C(=O)O-]$ ³⁾.

Recently the preparation of polyurethane using organic solvents is being restricted as well because the organic solvents are harmful for the atmosphere and their uses are regulated by law⁴⁾. Consequently, many researches have focused on the preparation and application of waterborne polyurethane (WPU) without contaminating the atmosphere^{5,6)}. Because the WPU does not form the chemical crosslinked structures, it has a weakness in the properties such as solvent and water resistance⁷⁾. Thus, in order to improve the resistivity for solvent or water, a scheme to form the crosslinked structures by the introduction of acrylic

group to polyurethane chain has been studied broadly⁸⁾. On the other hand, the studies of surface modification to give high performance polymer such as water repellence and the strain resistance by the introduction of fluorine group to polyurethane chain have also been conducted⁹⁾. Incorporation of fluorine into the polymer main chain or side chain is well known to lead to large changes of the surface properties as the fluorinated polymer chains segregates toward the polymer-air interface, resulting in considerable decrease in the surface energy^{3~8)}. The structures of the fluorinated polyurethane are strongly dependent on the preparation methods, the molecular structure of each segment, and their composition^{9,10)}. Especially, perfluoro-alkyl acrylate is used as processing agent for oil and water repellence and coating agent for water proof because it has convenient characteristic of translucent, low refractive index, and low surface energy¹¹⁾.

Several researchers have reported the modified polyurethane with respect to their chemistry, surface energy, and morphology. Yoon and Ratner¹²⁾ synthesized the fluorine modified polyurethane (FMPU) using fluorinated diol as a chain extender. Lim et al.¹³⁾ synthesized the FMPU using diisocyanate containing fluorine and investigated the surface and thermal property by

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mixing the polyurethane of ester form. Tonelli et al.^{14,15} synthesized the fluorinated polyurethane using polyol with fluorinated side chain and investigated the thermal property, dynamical property, morphology, and microstructure. Also, Kim et al.¹⁶ synthesized the FMPU using the fluorinated polyol and reported its surface property.

In this study, the waterborne perfluoroacrylic polyurethane composites (WFPUC) were prepared by two different methods, i.e. the emulsion polymerization and the physical blending. The surface and thermal properties of the WFPUC prepared by two methods were examined. The FA contents were varied to control the properties. The surface and thermal properties of WFPUC were investigated by the measuring the contact angle, surface energy, DSC, and TGA.

2. Experimental

2.1. Materials

Polyol used in this study was industrial grade polyester type diol with average molecular weight of 2000 and was used after demosture by the distilling methods. Hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) were purchased from Tokyokasei Corp.. They were used without further purification. Dimethylol propionic acid (DMPA) and di-n-butyltin (DBTDL) were the industrial grade purchased from LOJIT Corp. Triethyl amine (TEA) and n-methyl pyrrolidone (NMP) were the first grade purchased from Samchun Chemical Corp.

The perfluoroalkyl ethyl acrylate monomer (FA) was purchased from Daikin Corp. in Japan. Stearyl methacrylate (SMA) purchased from Aldrich Corp. and glycidyl methacrylate (GMA) purchased from LOJIT Corp. were used as polymerization aids. Ammonium persulfate (APS) used as initiator was purchased from LOJIT Corp.

2.2. Synthesis

The waterborne polyurethane (WPU) was prepared by neutralizing polyurethane prepolymer obtained by reacting polyol, isocyanate and ionomer¹⁷. The recipes for preparing WPU are shown in Table 1. A 2 L four-necked separated flask with a mechanical stirrer, a condenser, a dropping funnel, a nitrogen injector, and a thermometer was used as a synthesizing reactor. The reaction was carried out in a constant heating

Table 1. Recipes for the synthesis of WPU and FA emulsion

	Components	Amounts (wt%)
WPU	Polyester Diol	26.3
	HDI	4.6
	IPDI	2.6
	DMPA	1.1
	TEA	1
	Deionized water	64.4
FA emulsion	FA	14.7
	SMA	19.6
	GMA	1.6
	Surfactant	2.5
	Deionized water	61.6

mantle. A given amount of polyol was charged into four-necked flask and was completely dried using vacuum, and DMPA dissolved in NMP were added to the flask. The mixture was stirred for 1 hour at 90°C. After cooling, HDI, IPDI, and DBTDL were added, and the prepolymer was obtained by reacting for 3 hours at 70°C. Again, the temperature was lowered to 50°C, and the calculated amount of TEA was added. The mixture was neutralized with TEA and stirred for about 30 minute. Then, the ionized prepolymer was obtained. The WPU was prepared by adding deionized water to this ionized prepolymer with stirring at 300 rpm.

The FA emulsion was prepared by the emulsion polymerization method using surfactant. First of all, NMP was added into 250mL beaker together with FA, SMA, and GMA. The mixture was stirred for a given amount of time. The distilled water and surfactant were added in another beaker. The solutions of these two beakers were mixed and homogenized using ultrasonic homogenizer (BRANSON, SONIFIER 450) at 45°C.

The WFPUC were prepared by two different methods, i.e. the emulsion polymerization (WFPUC-E) and the physical blending (WFPUC-B). The WFPUC-E was prepared by the emulsion polymerization of WPU and FA, and its procedure was shown in Scheme 1. The ratio of adding FA was shown in Table 2. APS initiator dissolved in water was added at about 80°C using dropping funnel. After completely dropping it was reacted for 2 hours to synthesize the WFPUC-E. The WFPUC-E series were prepared by changing FA contents from 0.7 wt% to 13.2 wt% based on the

Table 2. Formulations of WFPUC-E and WFPUC-B series used in this study

Method	Samples	FA content (wt%)
Emulsion polymerization	WFPUC- E1	0.7
	WFPUC- E2	1.5
	WFPUC- E3	3.0
	WFPUC- E4	4.4
	WFPUC- E5	7.4
	WFPUC- E6	10.3
	WFPUC- E7	13.2
Physical blending	WFPUC - B1	0.7
	WFPUC- B2	1.5
	WFPUC- B3	3.0
	WFPUC- B4	4.4
	WFPUC- B5	7.4

total solid content.

The WFPUC-B was prepared by blending FA copolymer and WPU. The WFPUC-B series were prepared by changing the amounts of FA copolymers from 0.7 wt% to 13.2 wt%. The FA copolymer was synthesized by adding a constant amount of APS initiator into FA emulsion and by reacting them for 4 hours at 80°C.

2.3. Characterization

The molecular structures of WFPUC were characterized by using FT-IR-ATR spectroscopy (Perkin Elmer, IFS88). The thermal stability was measured using thermogravimetric analysis (TGA, Perkin Elmer, TGA 7) at the heating rate of 10°C/min from the room temperature to 700°C under nitrogen environment.

The surface property of WFPUC was characterized by measuring contact angle of cast film and estimating surface free energy from contact angle data. The films were prepared on a slide glass cleaned with the sulfuric acid solution and the distilled water. The wetting liquids used for contact angle measurement were water and n-dodecane. The contact angle was measured with contact angle analyzer (Pinics pro 300, SEO), and was performed by placing water and n-dodecane drops in different part of the prepared WFPUC film. The contact angles were measured five times for each sample at the room temperature and the average value for measurements was to be chosen.

3. Results and Discussion

Fig. 1 shows the IR spectra of (a) WFPUC-E2, (b) FA copolymer, and (c) WPU. In the case of WPU as

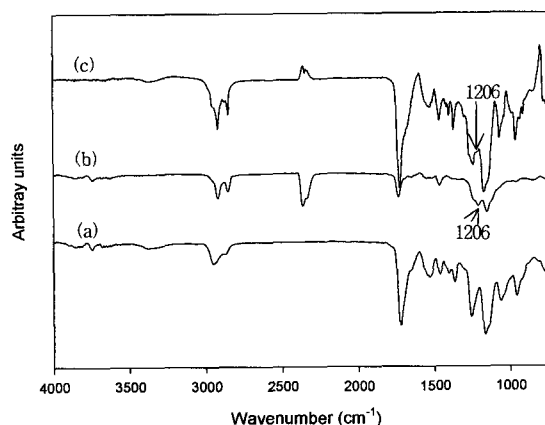


Fig. 1. FT-IR spectra of (a) WPU, (b) FA copolymer and (c) WFPUC-E2.

shown in Fig. 1(c), the regions of absorption peak lies at near 3,330 cm^{-1} and carbonyl specific peak of urethane lies at near 1,724 cm^{-1} . The band at 1,260 cm^{-1} and 1,173 cm^{-1} is attributed to the asymmetrical stretching and symmetrical stretching of CO- band of polyester, respectively. Through the IR spectra, the formation of WPU can be confirmed. Compared the IR spectra (b) with (a), the band at 1,260 cm^{-1} is associated with stretching vibration of the -CF-. Also, in the case of WFPUC-E as shown in Fig. 1(a), -NH- and carbonyl groups which are the specific peaks of WPU were observed, and -CF- specific peak of FA was appeared at 1,209 cm^{-1} .

Fig. 2 shows the ATR spectra of the surface of WFPUC-E film according to FA contents of 0.7 wt% to 13.2 wt% based on the total solid content. As FA content increased, -CF- absorption peak at 1,206 cm^{-1} increased. Moreover, for FA content of above 1.5 wt%, -CF- absorption peak increased significantly. This result implied that the fluorine content in WFPUC-E increased proportional to the addition of FA.

In order to investigate surface energy property, the contact angles on solid surface with two wetting liquids of water (polar component) and n-dodecane (dispersion component) were measured. Fig. 3 shows the increase of contact angle for water and n-dodecane emulsion with the increase of FA content. When water was used pure WPU film without FA copolymer had a contact angle of 70°. However, when FA content was 1.5 wt%, its contact angle increased up to 117°. When FA content in WFPUC-E was greater

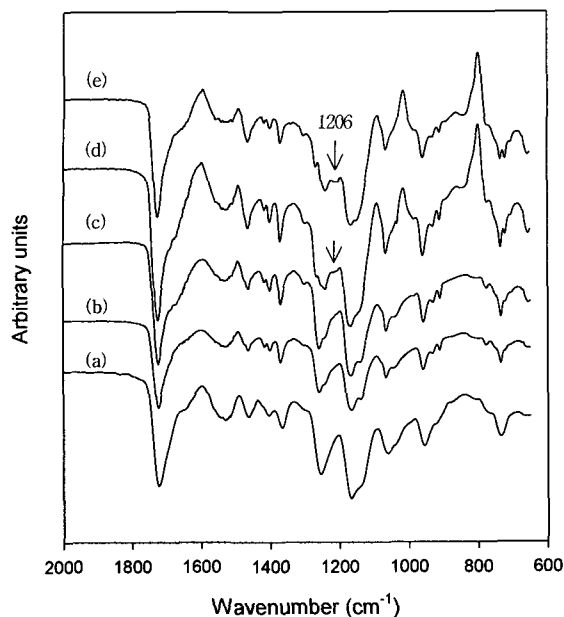


Fig. 2. FT-IR-ATR spectra of (a) WPU, (b) WFPUC-E1, (c) WFPUC-E2, (d) WFPUC-E3 and (e) WFPUC-E4.

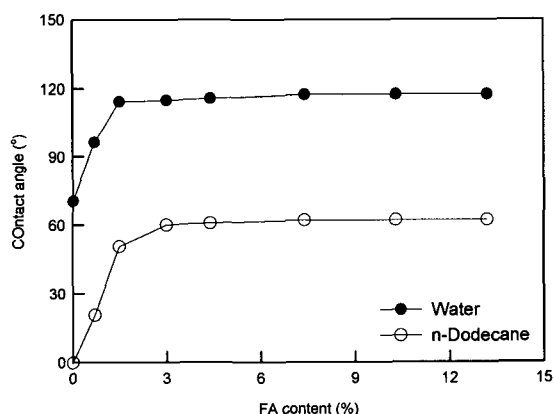


Fig. 3. Contact angle of WFPUC with different FA contents.

than 1.5 wt%, the water contact angle did not change and maintained relatively constant value. In the case of n-dodecane as liquid drop, the contact angle of WFPUC-E above 3.0 wt% of FA content was around 60° because of hydrophobicity of dodecane, but did not show any significant changes. This is because the surface is almost saturated by FA copolymer at FA content of above 3.0 wt%, and any great amount of fluorine addition would not affect the surface.

Table 3 shows the surface energy calculated from the contact angle data. The surface energies of films

Table 3. Surface energies of WFPUC series calculated by Owens-Wendt geometric method¹⁸⁾

Samples	Surface energy (mN/m)	Dispersion (mN/m)	Polar (mN/m)
WPU	37.54	25.35	12.19
WFPUC- E1	25.73	23.73	1.82
WFPUC- E2	17.04	16.93	0.11
WFPUC- E3	14.44	14.22	0.22
WFPUC- E4	14.13	13.88	0.25
WFPUC- E5	13.92	13.85	0.07
WFPUC- E6	13.90	13.81	0.09
WFPUC- E7	14.02	13.88	0.14

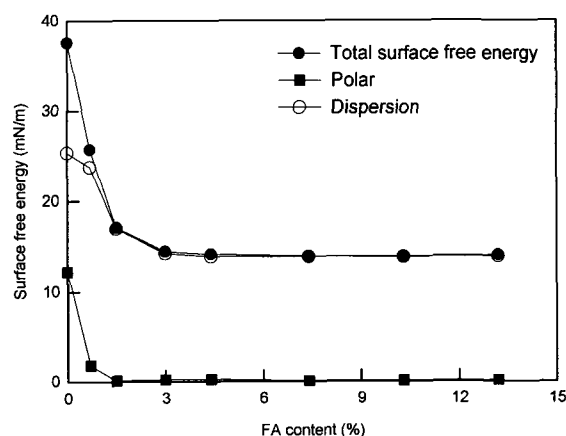


Fig. 4. Surface energy of WFPUC with different FA contents.

were calculated by Owens-Wendt equation¹⁸⁾ as follows:

$$\gamma_L(1 + \cos\theta) = 2(\gamma_L^D \times \gamma_S^D)^{1/2} + 2(\gamma_L^P \times \gamma_S^P)^{1/2} \quad (1)$$

where γ_L is the interfacial tension of the contact solution. γ_L^D and γ_L^P are the interfacial tension of the dispersion component and the polar component of the interfacial tension of solid, respectively. γ_S^D and γ_S^P are the interfacial tension of the dispersion component and the polar component of the surface tension of the wetting of liquid, respectively. θ is the contact angle of the specimen.

On comparing the surface energy of WPU and WFPUC-E2 as shown in Table 3 and Fig. 4, the surface energy significantly decreased from 37.54 mN/m to 16.93 mN/m. This phenomenon seemed to occur because the fluorine group of FA copolymer were being rapidly migrated towards the surface region of film. However, for FA content above 3.0 wt%, the

surface energy remained relatively constant as 13 ~ 14 mN/m because FA content on the surface was almost being saturated.

Fig. 5 compares the surface energy between the WFPUC-E and WFPUC-B films. Fig. 4 showed that when FA content was greater than 3.0 wt%, the surface energy of the WFPUC-E was 13 ~ 14 mN/m and was relatively constant. However, Fig. 5 shows that the surface energy of WFPUC-B decreased abruptly when FA content was less than 0.7 wt%; for FA content greater than 0.7 wt%, it remained constant at about 23 ~ 25 mN/m. Thus, the surface energy of WFPUC-E prepared from FA emulsion and WPU was lower than that of WFPUC-B blended with FA copolymer and WPU.

Fig. 6 and Fig. 7 show the FT-IR results of the upper side exposed to the air and of lower side un-

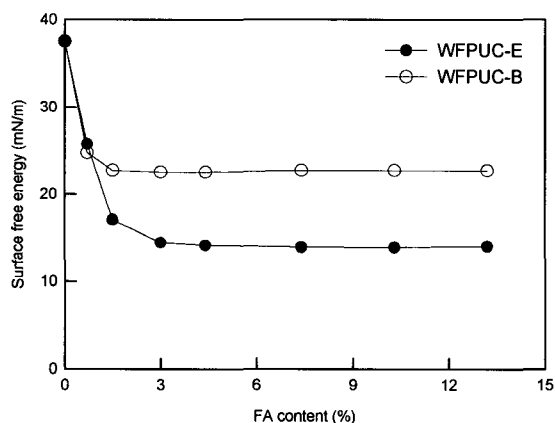


Fig. 5. Comparison of surface energy for WFPUC-E and WFPUC-B.

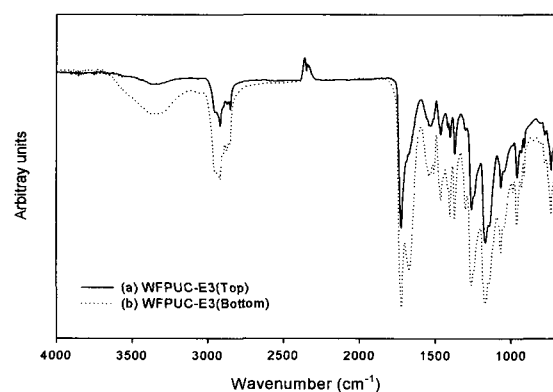


Fig. 6. FT-IR-ATR spectra of (a) top and (b) bottom of WFPUC-E3.

exposed to the air of the synthesized WFPUC-E and FA/WPU-B films, respectively. As shown in Fig. 6(b), -NH- peak at near 3,330 cm^{-1} and -CH- peak at 2,920 cm^{-1} in the lower side of WFPUC-E film, which was not exposed to the air, was comparatively greater than that in the upper side. In contrast, the measured ATR results (Fig. 6(a)) of the upper side that was exposed to the air showed that the -NH- and -CH- specific peaks of urethane seemed relatively weak and -CF- specific peak was observed at 1,210 cm^{-1} . These results might be possibly due to the hydrophobic fluorine being migrated towards the surface and hydrophilic urethane being migrated towards the subject matter.

As shown in Fig. 7, -NH- specific peak at near 3,330 cm^{-1} , -CH- specific peak at 2,920 cm^{-1} , and -CO- specific peak at 1,720 cm^{-1} , which these peaks were urethane specific peaks, were observed at both the upper and lower side of the film. Also, the -CF- peak which was FA copolymer specific peak was weakly found at 1,209 cm^{-1} . The surface energy for the case of WFPUC-E3 was very low and this is because hydrophobic fluorine group was being migrated towards the surface. However, WFPUC-B3 blended with WPU and FA copolymer had greater surface free energy than WFPUC-E3. This is because the surface migration of FA copolymer was suppressed by the interactions between WPU and FA copolymer.

The DTG curves of WPU, FA copolymer, WFPUC-E3 and WFPUC-B3 are shown in Fig. 8. Fig. 8(a) compares the thermal decompositions of WPU and FA

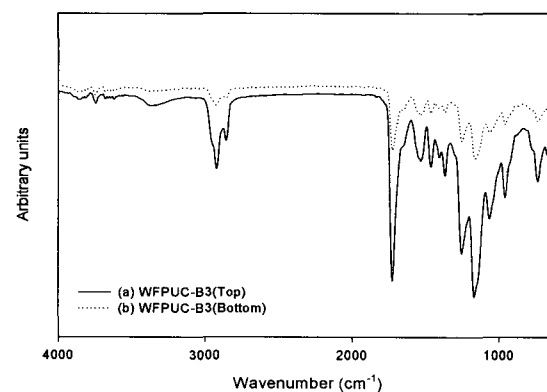


Fig. 7. FT-IR-ATR spectra of (a) top and (b) bottom of WFPUC-B3.

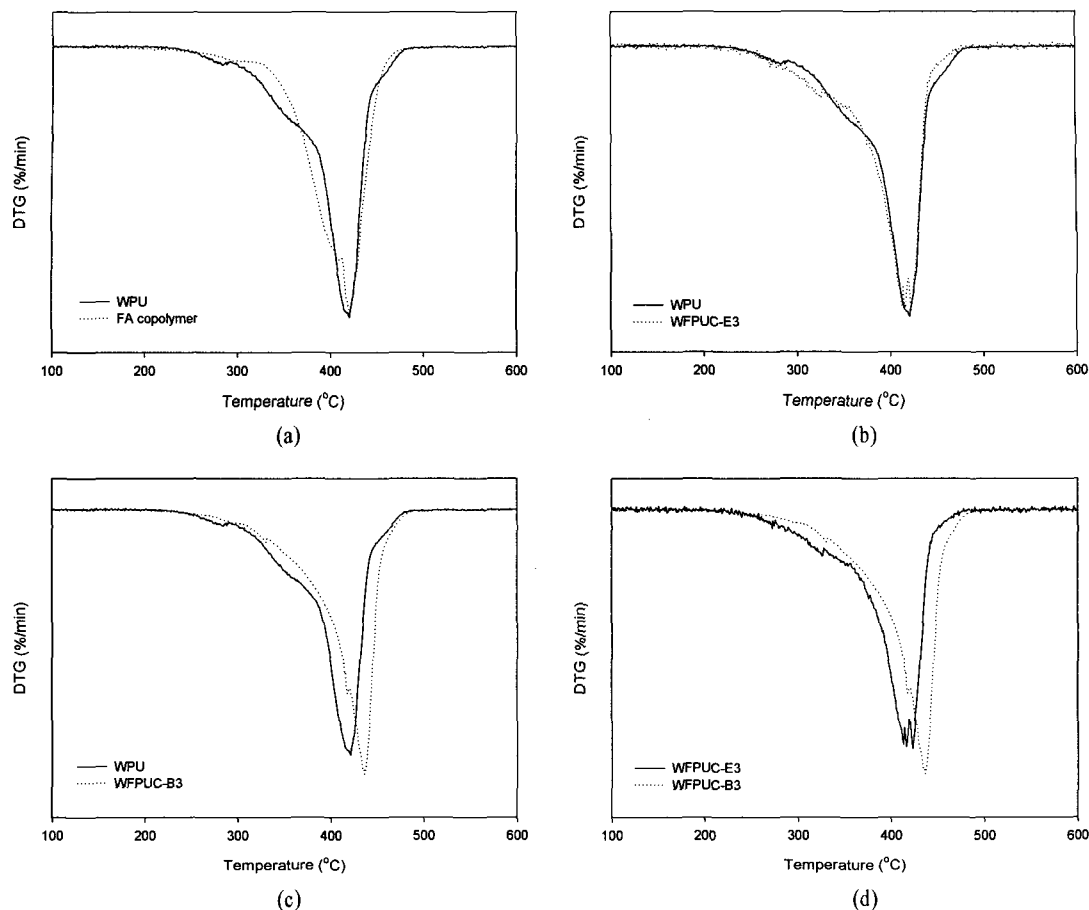


Fig. 8. DTG analysis of TGA thermograms of WPU.

copolymer. As shown in Fig. 8(a), the slope of WPU increased significantly near 285°C but the slope of FA copolymer increased near 340°C. This result showed that FA copolymer was thermally more stable than WPU. Fig. 8(b) shows that the slope of WFPUC-E3 was like that of WPU at the range between 285°C and 350°C but the shoulder around 350°C, in the case of WFPUC-E3 added FA emulsion, was disappeared and the thermal stability was somewhat increased. Fig. 8(c) shows that WFPUC-B3 blended with FA copolymer and WPU had higher thermal stability than WPU. Fig. 8(d) compares the DTG curves of WFPUC-E3 and WFPUC-B3. This figure showed that the thermal stability of the WFPUC-B prepared by the physical blending showed better than that of the WFPUC-E prepared by the emulsion polymerization. It was considered that the thermal stability was increased by the mutual chain entanglement between WPU and FA

copolymer.

Fig. 9 shows the TGA thermogram measured with changing FA content of WFPUC-E film. The maximum decomposition temperature which the weight decreased abruptly was verified by finding the maximum value in the differential curve of the thermal weight loss. From the observation of the thermal weight loss from 320°C to 420°C, WFPUC-E2 showed the greatest value of the thermal weight loss and its values decreased in the order of WFPUC-E3, WPU, WFPUC-E4, and FA copolymer. The WFPUC-E2 with FA content of 1.5 wt% had less thermal stability than WPU, but WFPUC-E3 with 3.0 wt% FA content had a similar tendency with WPU and had the characteristics of FA at the same time. These observations were also verified in Fig. 8(b). When FA content was greater than 3.0 wt%, the characteristics of FA affected highly and its thermal stability was better than

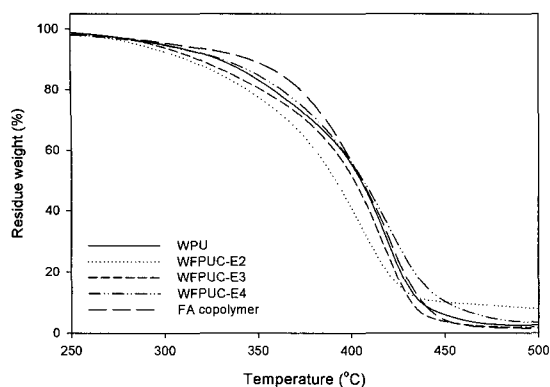


Fig. 9. TGA thermograms of WFPUC with different FA content.

that of WPU. When FA content was lower than 1.5 wt%, FA decreased the crystallinity of WPU and dropped the thermal stability.

4. Conclusions

The WFPUC series containing various FA contents were prepared by the emulsion polymerization (WFPUC-E) and the physical blending (WFPUC-B). The WFPUC-E was prepared by polymerizing FA and WPU, and WFPUC-B was prepared by blending FA copolymer and WPU. The structure of the prepared WFPUC was characterized using the FT-IR analysis, the specific peak -CF- of FA in WFPUC-E and WFPUC-B was found at $1,206\text{ cm}^{-1}$, and as FA content increased, -CF- peak increased. The surface energy of WFPUC-E decreased as FA content increased, and it was constant at $13 \sim 14\text{ mN/m}$ when FA content was greater than 3.0 wt%. By comparing the surface energies of WPU and WFPUC-B3, it was observed that the surface energy of WFPUC-B3 was greater than that of WPU. The WFPUC-E2 with FA content of 1.5 wt% had less thermal stability than WPU, but WFPUC-E3 with FA content of 3.0 wt% tended to have similar characteristics compared to WPU. For FA content greater than 3.0 wt%, the characteristics of FA had greater affect showing better thermal stability than WPU and dropped the thermal stability.

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