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Synthesis of Fluorinated Polyurethane/Polyacrylate Hybrid Emulsion Initiated by ^{60}Co γ-Ray and Properties of the Latex Film

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Based on the solvent-free method, novel fluorinated polyurethane/polyacrylate hybrid emulsions, dodecafluoroheptyl methacrylate (DFMA) as fluorinated monomer, were successfully prepared via emulsion polymerization without traditional emulsifier. For the purpose of increasing the grafting ratio of polyurethane and polyacrylate, ^{60}Co γ-ray radiation polymerization had been adopted to enhance the hardness of latex film. The chain structure and polymerization progress were confirmed by the analysis of Fourier transform infrared spectroscopy. The grafting ratio of polymethyl methacrylate and polyurethane was obtained by calculating the ratio of N–H peak integral area and Ph(C=C) peak integral area. The effect of DFMA content on thermal stability, mechanical property and water resistance were investigated systematically by thermal weight loss analysis, tensile strength test, absorbed water ratio and water contact angle.

Keywords: Solvent-free, hybrid emulsion, dodecafluoroheptyl methacrylate, grafting ratio,^{60}Co γ-ray

1 Introduction

It is known that waterborne polyurethane (WPU) is of low volatile organic compounds (VOC) emission or VOC-free. Due to good adhesion, elasticity, and chemical resistance, it has been applied in adhesives, coatings, and textile industries. However, the higher cost has limited its wide application. Meanwhile, polyacrylate (PA) is known as its wearing resistance, adjustable mechanical property and low cost. So the combination of WPU and PA (WPUA) is expected to be an effective way to reduce cost and retain their excellent properties; until now, a great deal of work has been focused on WPUA (1–9). It was proved that the vinyl group and epoxy group were attached to WPU to increase the grafting reaction probability between WPU and polyacrylate, which could improve the performance of WPUA composite material (10,11). In addition, the grafting reaction between polyurethane and polymethyl methacrylate (PMMA) had been investigated systematically by several groups (12–14).

However, by traditional chemical induced seeded-emulsion polymerization of acrylate with waterborne polyurethane stabilizer, the grafting ratio is not very high and the improvement of performance is limited. In our previous work (15), we had prepared a series of polyurethane/polyacrylate hybrid emulsion by using ammonium persulfate (APS) as initiator. The obtained films were soft and not suitable for surface coating. In this work, we had successfully prepared a series of polyurethane/polyacrylate hybrid emulsion by solvent-free method. Gamma rays from ^{60}Co source were used to initiate emulsion polymerization and we got solid content as high as 45% hybrid emulsions without additional initiators. It was expected that this initiation method could increase grafting ratio and hardness of latex film. Adding a certain content of novel fluorinated acrylate monomer-dodecafluoroheptyl methacrylate to modify polyurethane/polyacrylate (FWPUA) has also been chosen to enhance water resistance and thermal stability.

2 Experimental

2.1 Materials

Polytetramethylene glycol (PTMG), $M_n = 2000$, Daicel Chemical Industries, Ltd.; toluene diisocyanate (TDI)

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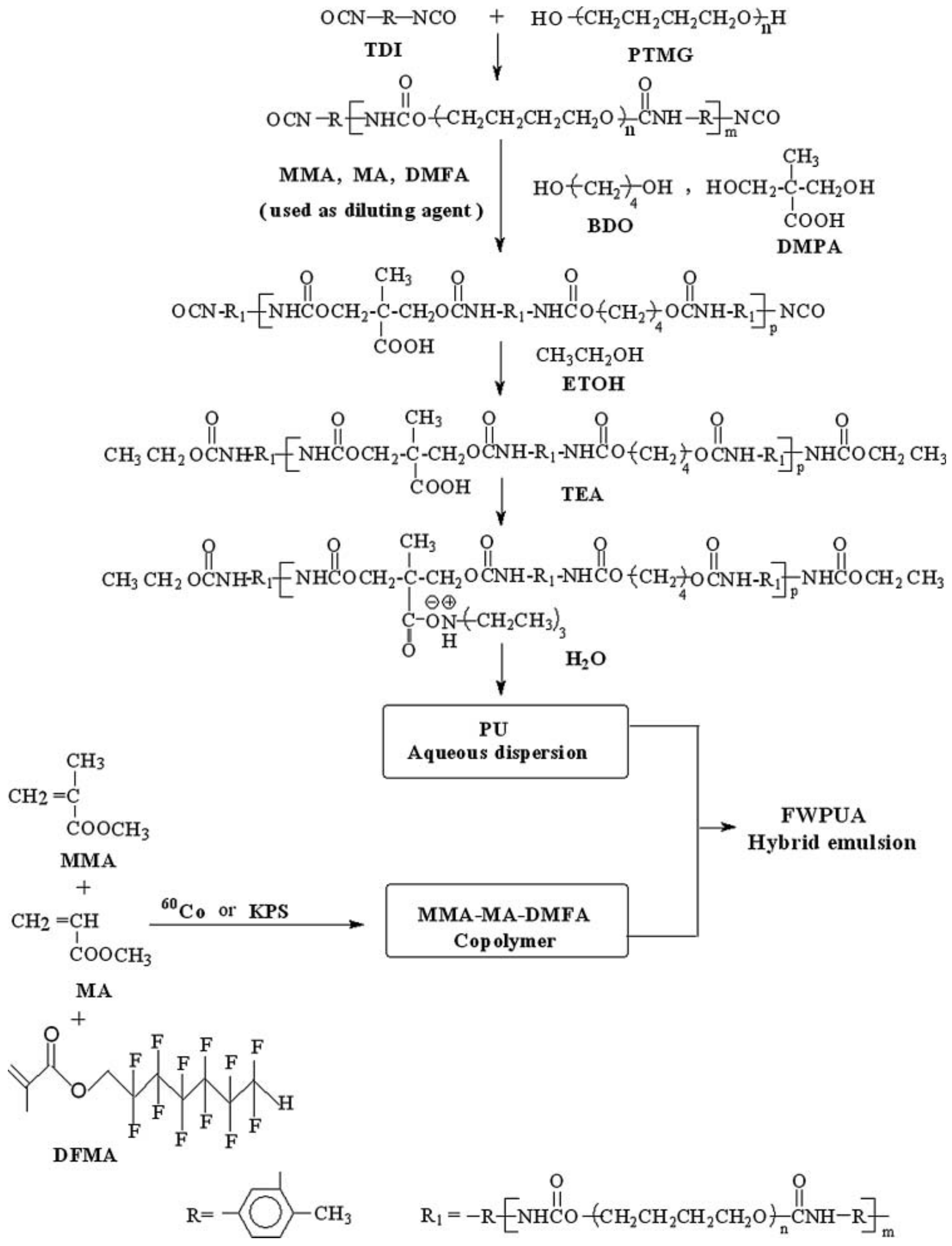

Fig. 1. Preparation process of FWPUA hybrid emulsion.

and dimethylol propionic acid (DMPA) were the products of Aldrich Chemical Company; ethanol (ETOH), methyl methacrylate (MMA), methacrylate (MA), butanediol (BDO), potassium persulfate (KPS) used as initiator, triethylamine (TEA) used as neutralization agent, sodium bicarbonate ($NaHCO_3$) used as pH buffer solution and di-*n*-butyltin dilaurate (DBT) used as catalyst were all purchased from Shanghai Chemical Reagent Co., Ltd.; hydroquinone was used as an inhibitor, Luoyang Chemical Reagent Company; dodecafluoroheptyl methacrylate (DFMA) was purchased from Ivy Fine Chemicals Co., Ltd.; DMPA, PTMG and BDO were vacuum desiccated and TDI was vacuum distilled before using. DFMA, MA and MMA were used as received.

2.2 Synthesis of FWPUA

The hybrid emulsion of FWPUA was prepared according to the procedure shown in Figure 1. TDI and PTMG were first added into a dry vessel equipped with a reflux condenser, a mechanical stirrer and a thermometer. The polymerization of polyurethane was carried out at 85°C under N_2 atmosphere until the NCO content reached a theoretical value. Then, DMPA, BDO and an inhibitor were added into the system and reacted at 75°C for 2 h. At the same time, a suitable amount of acrylate monomer was needed to reduce the viscosity of prepolymer. Next, the catalyst DBT and single-hydroxyl alcohol ETOH were added to terminate the polyurethane at 70°C until the NCO group

Table 1. Compositions for WPUAs

Sample code	*TDI: PTMG: DMPA: BDO: TEA*: ETOH (mol: mol)*	*MMA/(MA+MMA) (wt%)*
WPUA1	1:0.24:0.32:0.39:0.35:0.05	0
WPUA2	1:0.24:0.32:0.39:0.35:0.05	16.67
WPUA3	1:0.24:0.32:0.39:0.35:0.05	33.33
WPUA4	1:0.24:0.32:0.39:0.35:0.05	50
WPUA5	1:0.24:0.32:0.39:0.35:0.05	66.67
WPUA6	1:0.24:0.32:0.39:0.35:0.05	83.33
WPUA7	1:0.24:0.32:0.39:0.35:0.05	100

*mole ratio of TEA:DMPA is fixed at 1.1:1 to secure full neutralization.
**mass ratio of WPU:PA is fixed at 1:0.8.

had been totally consumed. As a neutralization agent, TEA was added to react with carboxylic group in the side chain of the polymer, and the mole ratio of TEA to DMPA was fixed at 1.1:1 to secure the 100% neutralization degree. Afterward, a high speed shearing rate (5600 r/min) was used to emulsify the solution for 5 min followed by suitable deionized water which was added into the reaction system. The polyurethane aqueous dispersion containing acrylate monomer was obtained.

Then, the resultant aqueous dispersion was purged with nitrogen for 10 min to remove the dissolved oxygen in the system. The next step continued, the aqueous dispersion was irradiated by ^{60}Co γ-ray at a dose rate of 106.5 Gy/min for 6 h at room temperature or KPS aqueous solution was added dropwise to the system while $NaHCO_3$ was used to maintain pH value and the reaction lasted for 6 h at 80°C. Finally, the emulsion was cooled down to room temperature and DFMA modified waterborne polyurethane/polyacrylate hybrid emulsion (FWPUA) was obtained. In order to compare the properties of synthesized materials, some WPUAs with different MA (or MMA) content were synthesized and the compositions are shown in Table 1. By changing the material ratio, a series of FWPUAs with different DFMA content, as shown in Table 2, were also synthesized.

2.3 Sample Preparation and Characterization

A thin latex film (thickness less than 20 μm) for FTIR was directly fixed on a sample frame and measured ranging from 500 to 4000 cm^{-1} with a Nicolet Magna-IR 750 FTIR spectrometer.

The latex films were prepared by casting the hybrid emulsion on a leveled PTFE plate, cured at room temperature for 7 days and then vacuum dried at 60°C to a constant weight. The films were prepared for further investigation, with the thickness of 0.2 mm.

A tensile strength test was carried out on a tensile tester (Model TY8000, Jiangdu Tianyuan Test Machine Co., Ltd., China) at room temperature with a speed of 50 mm·min^{-1}. All measurements have an average of 4 runs. The dumbbell type specimen was 30 mm length at two ends, 0.2 mm thickness and 4 mm wide at the neck.

Pendulum hardness of latex film was measured according to the Chinese-standard GB/T 1730-93 of determination of hardness of the paint films-pendulum damping test.

The thermal stability of FWPUA latex film was followed by using thermalyzer DT-50 (Shimadzu Corporation, Japan) at temperatures from 25 to 600°C and with 10°C min^{-1}heating rate in N_2 atmosphere.

The contact angle of water droplets on the latex film was measured by a contact angle goniometer (JC2000C1, Shanghai Zhongchen Digital Technical Equipment Ltd., China), and the reported results were the mean values of five times.

The water resistance property was characterized by the absorbed water ratio of latex film immersed into water. W_0 g latex film was immersed into distilled water at room temperature for 24 h, and W_1 g film absorbed water was obtained by wiping off surface water with a piece of filter paper. The absorbed water ratio could be calculated according to the formula:

$$W(\%) = (W_1 - W_0)/W_0 \times 100\%$$

3 Results and Discussion

3.1 Analysis of FTIR Spectra

The polymerization progress of FWPUA sample was monitored by FTIR spectra. As shown in Figure 2, the curve "a" is symbolized as polyurethane prepolymer curve with

Table 2. Compositions for FWPUAs

Sample code	*TDI:PTMG:DMPA:BDO:TEA*:ETOH (mol:mol)*	*DFMA/(MMA+DFMA) (wt%)*	*latex film appearance*
FWPUA O	1:0.24:0.32:0.39:0.35:0.05	0	transparent
FWPUA 1	1:0.24:0.32:0.39:0.35:0.05	6.7	transparent
FWPUA 2	1:0.24:0.32:0.39:0.35:0.05	13.3	transparent
FWPUA 3	1:0.24:0.32:0.39:0.35:0.05	20	transparent
FWPUA 4	1:0.24:0.32:0.39:0.35:0.05	26.6	transparent
FWPUA 5	1:0.24:0.32:0.39:0.35:0.05	33.3	semitransparent
FWPUA 6	1:0.24:0.32:0.39:0.35:0.05	40	semitransparent

*mole ratio of TEA:DMPA is fixed at 1.1:1 to secure full neutralization.
**mass ratio of WPU:PA is fixed at 1:0.8.

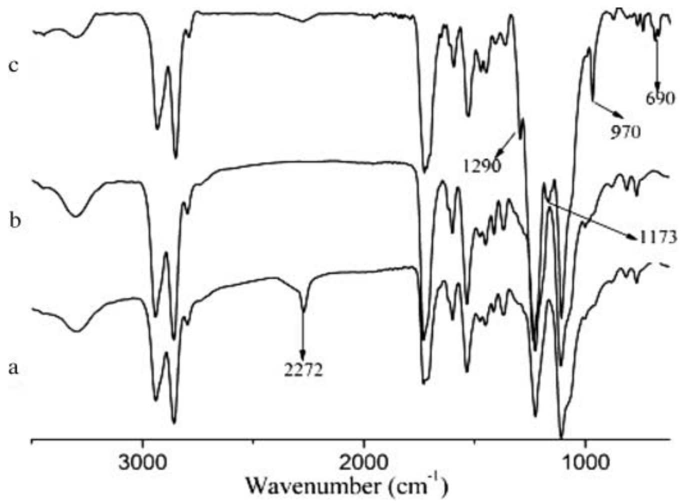

Fig. 2. FTIR spectra of FWPUA sample. (a) Before adding ETOH; (b) 5.5 h after adding ETOH; (c) after emulsion polymerization.

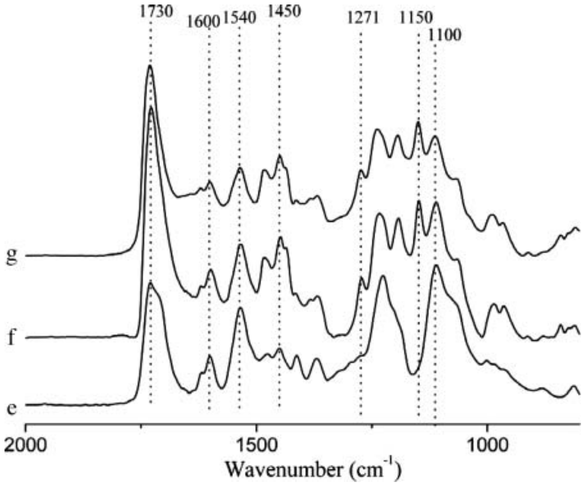

Fig. 3. FTIR spectra of WPUA with different initiation methods: (e) WPU; (f) WPUA initiated by KPS; (g) WPUA initiated by ^{60}Co γ-ray.

NCO group because ETOH had not been added into the system; we could clearly observe the sharp and strong NCO absorption peak around 2272 cm^{-1}. After adding a suitable amount of ETOH 5.5 h later, the NCO peak in the curve "b" completely disappeared, indicating that the NCO group in PU had reacted with the OH group in ETOH to form the —NH—COO—group, and the polymerization of polyurethane was completed. The absorption peaks of typical polyurethane at 3330 cm^{-1} [ν(NH)], 2855–2955 cm^{-1} [$\nu(CH_2)$] and [$\nu(CH_3)$], 1720–1780 cm^{-1} [ν(C=O)], 1540 cm^{-1} [δ(NH)] and 1110 cm^{-1} [ν(C–O–C)] can be seen clearly in the spectra. The absorption peak at 1600 cm^{-1} is attributed to typical peak of Ph(C=C) group belonging to TDI. The curve "c" shows that DFMA monomers had been copolymerized. The absorption peaks of C–F bond at 690 cm^{-1} (CF_2rocking), 1173 cm^{-1} [$\nu_s(CF_2) + \delta(CF_2)$] and 1290 cm^{-1}[$\nu_a(CF_2) + \gamma(CF_2)$] demonstrate further that DFMA had been incorporated into the polymer chains. In addition, a distinct absorption peak at 970 cm^{-1}presenting the absorption of C–H (CF_2CF_2H) also appeared in the spectra of FWPUA.

Figure 3 also illustrates FTIR spectra of WPUA samples with different initiation methods. The characteristic absorption of the C=C bond at 1640 cm^{-1} disappeared, indicating that the acrylic monomers had been polymerized. The absorption peaks at 1271 cm^{-1} [ν(C—O)] and 1150 cm^{-1}[ν(C—O—C)] of ester are the typical absorption peaks for the spectra of PMMA. At the same time, the increase of absorption at 1450 cm^{-1} [δ(C—H)], 1730 cm^{-1} [ν(C=O)] also confirmed polyacrylate structure. In the emulsion polymerization process, the mechanism of grafting reaction between polyurethane and polymethyl methacrylate is shown in Figure 4. It is known that the characteristic Ph(C=C) group belonging to TDI around 1600 cm^{-1} has no change during the entire emulsion polymerization process, and it could be used as a reference group in the calculation of relative N–H peak integral area change to calculate the grafting ratio of PMMA and WPU. The ratios of N–H peak integral area and Ph(C=C) peak integral area were shown in Figure 5. Compared to the original relative N–H (1540 cm^{-1}) peak area of WPU, it was found that the relative integral area of N–H peak apparently decreased

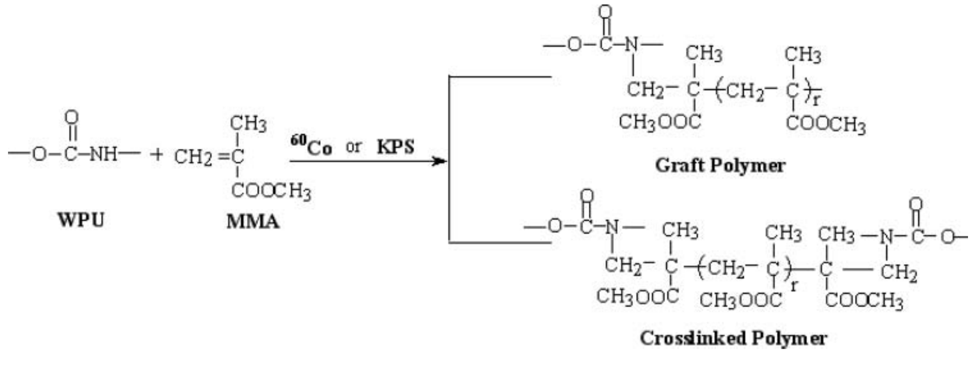

Fig. 4. Grafting reaction between polyurethane and polymethyl methacrylate.

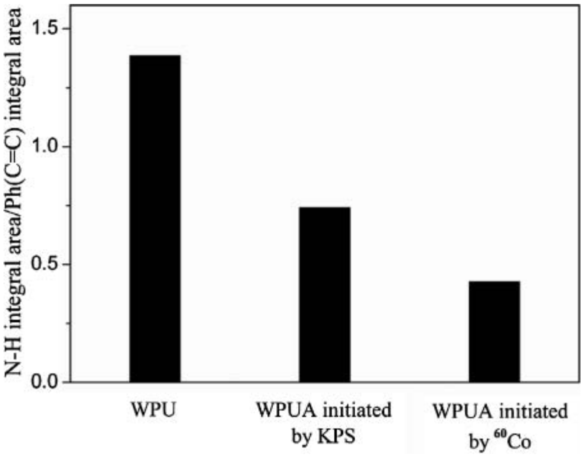

Fig. 5. The ratios of integration area with different initiation methods.

after emulsion polymerization. The relative N–H peak integral area of WPUA initiated by ^{60}Co γ-ray is less than that initiated by KPS. It could be attributed to the fact that a large number of radicals were produced in the gamma ray field. These reactions could enhance the grafting reaction probability between PMMA and WPU. So the grafting ratio of polyurethane and polyacrylate in ^{60}Co γ-ray initiated emulsion polymerization is larger than that initiated by KPS.

3.2 Pendulum Hardness

Pendulum hardness is one of the important physical properties of WPUA film that is taken into account for applications. The pendulum hardness of WPUA films with different MMA content and different initiation methods was investigated. Figure 6 shows that by keeping the mass ratio of polyurethane and polyacrylate unchanged while increasing the ratio of MMA/(MA+MMA), the pendulum hardness of latex film increases sharply. Because MMA is a more rigid monomer compared with MA, the copolymer with more MMA component becomes harder for its less activity. It also shows that the pendulum hardness of WPUA latex film initiated by ^{60}Co γ-ray is higher than that initiated by KPS. The increase of pendulum hardness could be attributed to the higher grafting ratio of polyacrylate and polyurethane which would generate more graft polymer and crosslinked polymer to form polymer network. Due to those grafting reaction and polymer networks, the activity of molecular chain is limited and the hardness of latex film increases.

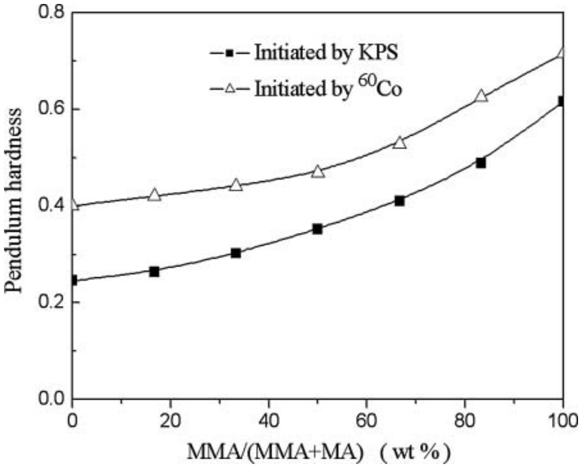

Fig. 6. Pendulum harness increases with increasing the MMA content for WPUA samples.

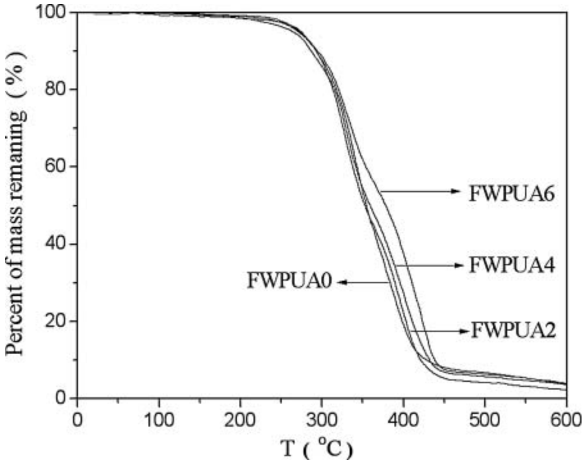

Fig. 7. The thermogravimetric curves of FWPUA samples.

3.3 Thermogravimetric Analysis

Figure 7 shows the TGA curves of a series of FWPUAs under N_2 atmosphere.. It could be clearly seen that the thermal stability of latex film increases with the increase of DFMA content. It is known that the chemical bond of C–F is more stable under high temperature. For the samples with different DFMA content, the different C–F bond densities of latex films lead to the differences in decomposition curves. The higher ratio of DFMA content, the better thermal stability of latex film. It could be found that introducing DFMA into WPUA as soft segment would improve the thermal stability of latex film.

3.4 Mechanical Properties

It is known that polydodecafluoroheptyl methacrylate is very flexible and tough, but has poor compatibility with other polymer materials. The excess incorporation of DFMA into polyacrylate copolymer is likely to decrease the tensile strength and the extensibility of latex film. Figure 8 shows that by keeping the mass ratio of polyurethane and polyacrylate unchanged and increasing the mass ratio of DFMA/(DFMA + MMA), the tensile strength and the extensibility of latex film would decrease while the mass ratio

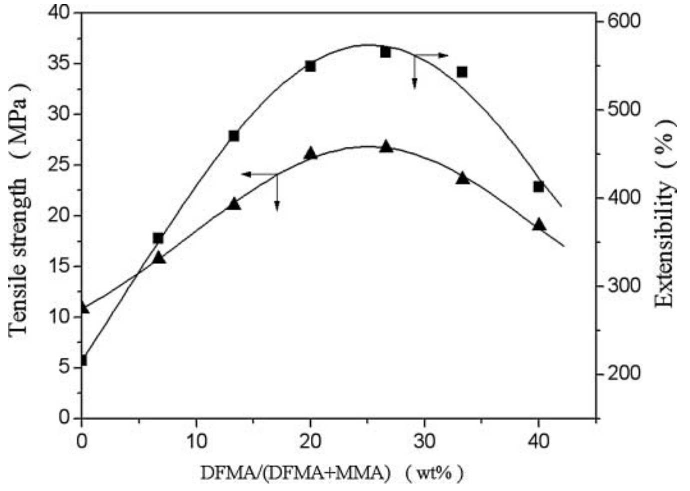

Fig. 8. The mechanical property for the FWPUA film.

of DFMA/(DFMA + MMA) exceeds 26.6%. It could be seen that FWPUA4 has the maximum of mechanical properties with extensibility of 566% and tensile strengths of 26.7 MPa. Since the latex film appearance of FWPUA5 and FWPUA6 is semi-transparent, it may be concluded that superfluous DFMA would cause microphase separation and decrease of mechanical properties at some degree.

3.5 The Water Contact Angle Analysis

As shown in Figure 9, there is a dependency relationship between water contact angle of FWPUA latex film and DFMA content. It is clearly observed that the water contact angle of FWPUA latex film increases with the increase of DFMA content. Generally, the surface water–air contact angle measurements are more surface-sensitive, probably responding to the outermost monolayer of surface. The increase of contact angle could be attributed to the migration of fluorinated groups. It was reported that hydrophobic character and oil repulsion of fluorinated polymer is not affected by polyurethane as emulsifier and fluorinated groups would migrate onto the outmost surface during the formation of film (16,17). It is also found that, when DFMA content is low, the curve ascends sharply. While with the increase of DFMA content, the contact angle becomes nearly constant. This is because there are enough fluorinated groups on the surface, the low surface free energy is close to the limit point.

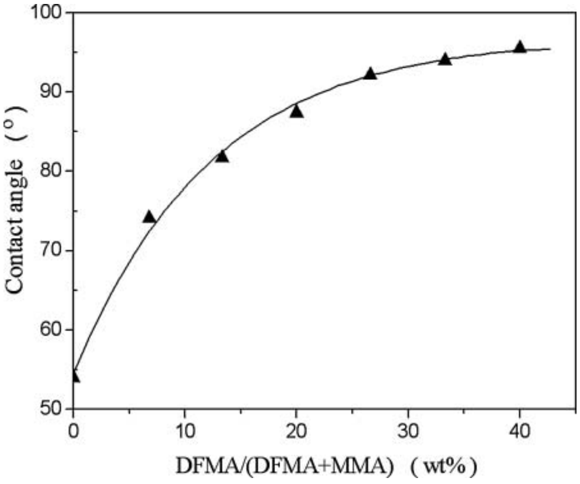

Fig. 9. Water contact angle increases with increasing the content of DFMA for FWPUAs.

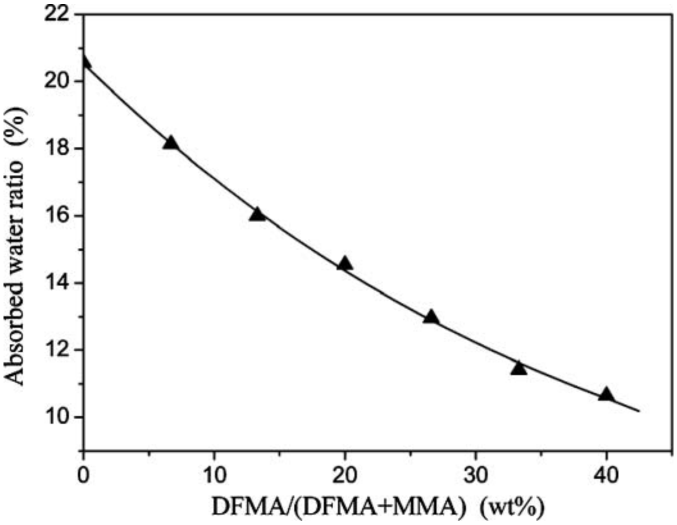

Fig. 10. Absorbed water ratio decreases with increasing the content of DFMA for FWPUAs.

3.6 The Water-Resistance Property

Correlation between absorbed water ratio and DFMA content for FWPUA samples is shown in Figure 10. It is observed clearly that the absorbed water ratio decreases with the increase of DFMA content. Fluorinated polymer has an obvious influence on absorbed water ratio. When DFMA/(DFMA + MMA) increases from 0 to 40%, the absorbed water ratio decreases from 20.6% to 10.7% and the water absorption capacity of latex film decreases sharply. It could be inferred that the migration of hydrophobic fluorinated groups would enhance water-resistance of FWPUA materials.

4 Conclusions

A series of FWPUA samples with different DFMA content had been synthesized by a solvent-free method. In this method, acrylate monomers acted as dilution agent and WPU with carboxy group acted as macromolecular emulsifier, without using any other solvent and emulsifier. The chain structure and grafting reaction were confirmed by FTIR analysis. The ratios of N–H peak integral area and Ph(C=C) peak integral area proved that ^{60}Co γ-ray radiation polymerization could enhance the grafting reaction probability between PMMA and WPU. By measuring the pendulum hardness, it was found that the increase of MMA content or choosing ^{60}Co γ-ray radiation polymerization could both enhance hardness of latex film. The DFMA content had a significant impact on mechanical property and thermal stability of FWPUA latex film. The investigation of water contact angle and absorbed water ratio indicated that the incorporation of DFMA could improve water resistance.

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References

1. Kukanja, D., Golob, J. and Krajnc, M. (2002) *J. Appl. Polym. Sci.*, 84, 2639–2649.
2. Dong, A.J., An, Y.L., Feng, S.Y. and Sun, D.X. (1999) *J. Colloid Interface Sci.*, 214, 118–124.
3. Dong, A.J., Feng, S.Y. and Sun, D.X. (1998) *Macromol. Chem. Phys.*, 199, 2635–2640.
4. Zhu, X.L., Jiang, X.B., Zhang, Z.G. and Kong, X.Z. (2008) *Prog. Org. Coat.*, 62, 251–257.
5. Dai, J.B., Zhang, X.Y., Chao, J. and Bai, C.Y. (2007) *J. Coat. Technol. Res.*, 4, 283–288.
6. Chen, L. and Chen, S. (2004) *Prog. Org. Coat.*, 49, 252–258.
7. Tsavalas, J.G., Gooch, J.W. and Schork, F.J. (2000) *J. Appl. Polym. Sci.*, 75, 916–927.
8. Kim, B.K. and Shin, J.H. (2002) *Colloid. Polym. Sci.*, 280, 716–724.
9. Hirose, M., Kadowaki, F. and Zhou, J.H. (1997) *Prog. Org. Coat.*, 31, 157–169.
10. Zhang, H.T., Huang, H. and Cao, J.H. (2004) *J. Appl. Polym.Sci.*, 94, 1–8.
11. Kukanja, D., Golob, J., Zupancic-Valant, A., and Krajnc, M. (2000) *J. Appl. Polym. Sci*, 78, 67–80.
12. Zhang, H.T., Guan, R., Yin, Z.H. and Lin, L.L. (2001) *J. Appl. Polym. Sci.*, 82, 941–947.
13. Kim, I.H., Shin, J.S., Cheong, I.W., Kim, J.I. and Kim, J.H. (2002) *Colloids Surf. A: Physicochem Eng. Asp.*, 207, 169–176.
14. Nair, P.D. and Krishnamurthy, V.N. (1996) *J. Appl. Polym. Sci.*, 60, 1321–1327.
15. Zhang, C.Y., Zhang, X.Y., Dai, J.B. and Bai, C.Y. (2008) *Prog. Org. Coat.*, 63, 238–244.
16. Li, G.H., Shen, Y.D. and Ren, Q.H. (2005) *J. Appl. Polym. Sci.*, 97, 2192–2196.
17. Jiang, M., Zheng, Z.H., Ding, X.B., Cheng, X. and Peng, Y.X. (2007) *Colloid. Polym. Sci.*, 285, 1049–1054.