Surface properties of latex film and solvent-borne film resulted from fluorinated acrylate copolymers prepared by emulsion polymerization

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Abstract. The fluorinated acrylate copolymer, poly (BMA-co-DFHMA), was prepared by emulsion polymerization using a preemulsified monomer addition process. The FTIR and ^1H -NMR were used to characterize the copolymer structure. The contact angle of water on the solvent-borne film increased dramatically and reached an equilibrium value (103°) when the PDFHMA content in the copolymer was only 0.97 mol%. However, the contact of water on the latex film increased slowly, and reached the equilibrium value of 99° until the fluorinated component content was as highly as 9 mol%. A similar result was observed for the oil contact angle on the two types of films. XPS results showed that when the F/C ratio on film surfaces reached equilibrium, the required content of fluorinated component in the copolymer for the solvent-borne film was much lower than that for the latex film.

Keywords: coatings, fluorinated acrylate, surface property, emulsion polymerization

1. Introduction

Due to their low surface free energy and chemical stability in a variety of environments, fluorinated polymers have been widely used as surface coatings of solid materials, such as water and oil repellents for the textile, protection materials for leather and stone, mold releasing agent, and so on [1–4]. Generally, the fluorinated polymers were prepared traditionally by solution polymerization for the theoretical research. However, from the viewpoint of practical applications, it is more desirable to synthesize fluorinated polymer latex. Compared to traditional solvent-base fluorinated polymers, the latex containing fluorine exhibits a variety of advantages such as non-inflammability, non-toxicity, and environmental friendly properties. Until recently, however, the preparation and film-forma-

tion of fluorinated polymer or copolymer latex has been paid attention [5–9].

It is well known that the monomers containing fluorine have relatively high price, the incorporation of large amount of fluorinated monomers in the copolymers would impair their market competition. Therefore, it is of great importance to reduce fluorinated component content in copolymers while keeping the excellent surface properties of the resulting copolymer films. Furthermore, it is very necessary to know the influence of the types of the obtained film, i.e. latex film and solvent-borne film, on their surface properties. Unfortunately, such investigation is seldom reported according to our knowledge.

In this paper, a series of fluorinated acrylate copolymers with different content of fluorinated components were prepared by emulsion polymer-

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ization, and the surface properties of the latex film and solvent-borne film were examined. The results showed that the solvent-borne film exhibited much more excellent water and oil repellency than the latex film.

2. Experimental

2.1. Materials

Dodecafluorheptyl methacrylate (DFHMA) was purchased from XEOGIA Fluorine-Silicon Chemical Company, Harbin, China. Its purity was above 97% and used without further purification. The structure of DFHMA was shown in Figure 1. Butyl methacrylate (BMA) was washed by 5 wt% sodium hydroxide solution to remove inhibitor, and then was distilled under reduced pressure. The water-soluble initiator (potassium persulfate, $K_2S_2O_8$) and emulsifiers including sodium dodecyl sulfate (SDS) and dodecyl polyoxy ethylene (OP-10) were used without further purification. The dionized water was obtained by ion exchange. Other chemicals were of reagent grade and used without further purification.

Figure 1. Schematic representation of the DFHMA

2.2. Emulsion polymerization

Emulsion polymerization was carried out in a 100 ml reactor using a typical preemulsified monomer addition process [10]. A typical recipe is: BMA, 20 g; $K_2S_2O_8$, 0.115 g; SDS, 0.07 g; OP-10, 0.18 g; dionized water, 46.7 g. The mol ratio of DFHMA to BMA was changeable and the solid content of the final latex remained about 25 wt%. The synthesis of the poly (BMA-co-DFHMA) latex was performed as follows: part of water, emulsifiers and initiator, and all monomers were emulsified for 30 min by stirring. The obtained monomer emulsion was then charged successively for 2 h into the reactor containing the remaining water, emulsifiers, and initiator at 80°C. After completion of monomer feeding, the reaction lasted for another 2 h.

2.3. Film formation

Latex films were prepared by spreading latexes directly on pre-cleaned glass slides. The films were allowed to dry at 60°C for at least 12 h. For the preparation of the solvent-borne film, the obtained latex particles were firstly precipitated in 5 wt% $CaCl_2$ solution. The obtained precipitates were washed with water several times after filtration. Next, the precipitates were dried under reduced pressure at 40°C. Finally, the dried precipitates were dissolved in cyclohexanone, and the resultant solution was cast on the glass slide. After evaporating the solvent, the solvent-borne film was obtained.

2.4. Characterization

The chemical compositions of the latex particles were determined by a Nicolet Aratar 370 FTIR spectrometer and a Bruker Advance AMX-400 NMR instrument using $CDCl_3$ as solvents. The contact angle on the film surface was measured by the sessile drop method [11] using a KRÜSS (Hamburg, Germany) DSA 10 goniometer. The contact angle reported in this work is the average of the values obtained from at least 8 different points on the film surface. The experimental error for contact angle measurement is within the range of $\pm 1^\circ$. The surface chemical compositions of the films were determined by X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA system, Perkin-Elmer) with a Mg $K\alpha$ X-ray source (1253.6 eV).

3. Results and discussion

3.1. Characterization of the fluorinated acrylate copolymers

Figure 2 shows the FTIR spectra of (a) poly (BMA-co-DFHMA) and (b) PBMA, respectively. Comparing the FTIR spectra (a) with (b), two new absorption bands are emerged at 692 and 706 cm^{-1} , which was due to the rocking and wagging vibrations of CF_2 groups [12]. In addition, the absorption bands at 1180 and 1220 cm^{-1} are attributed to the C–F bond stretching vibrations [5, 8]. Figure 3 shows the 1H -NMR spectrum of poly (BMA-co-DFHMA). The peak at 4.3 and 3.9 ppm are observed, which is assigned to the $-OCH_2-$ of DFHMA and BMA, respectively [12]. By evaluating the peak intensities at 4.3 and 3.9 ppm, the mol

Figure 2. FTIR spectra of (a) poly (BMA-co-DFHMA) and (b) PBMA. The content of DFHMA in the copolymers is 9.5 mol%

fraction of PDFHMA components in the copolymers can be determined. Moreover, it was found that the prepared poly(BMA-co-DFHMA) was soluble in tetrahydrofuran (THF). This suggested the polymer used in this study was a copolymer since the DFHMA homopolymer could not be dissolved in THF. These results above also indicate that the DFHMA have copolymerized with BMA.

3.2. Surface property of fluorinated acrylate copolymer film

It is well known that fluorinated components content in the copolymers has a significant effect on their surface properties. Figure 4 presents the con-

Figure 3. ^1H -NMR spectrum of poly (BMA-co-DFHMA). The content of DFHMA in the copolymers is 9.5 mol%

tact angle of water and paraffin oil on the latex film and solvent-borne film as a function of DFHMA content in the resulting copolymers. As shown in Figure 4a, the contact angle of water on solvent-borne film enhances dramatically from 88.1 to 103° when the DFHMA content increases from 0 to 0.97 mol%, in which the contact angle of water on latex film shows a little increase, i.e. from 81 to 84°. On the other hand, the contact angle of water on solvent-borne film reaches equilibrium when the

Figure 4. Contact angle of (a) water and (b) paraffin oil as a function of the mole fraction of PDFHMA in the resulting copolymer

DFHMA content is about 5 mol%. However, 9 mol% of DFHMA is required for the contact angle of water on latex film to reach equilibrium. When reaching equilibrium, the contact angle of water for the solvent-borne film is about 103° , whereas that for the latex film is only 99° . Similar results are observed for the contact angle of paraffin oil on the two types of films (see Figure 4b). Obviously, there exists a great difference in surface properties between the solvent-borne film and latex film. Furthermore, it is noted that at low level of fluorinated components, (e.g. lower than 5 mol%), the solvent-borne film exhibits much more excellent water and oil repellency than latex film although both of them have the same chemical composition.

Surface properties of materials are usually governed by the structure and chemical composition of the surface layer. In order to understand well the water and oil repellency of the resulted fluorinated acrylate film, the surface chemical compositions on the two types of films were examined by XPS. Shown in Figure 5 are F/C ratios for a series of poly (BMA-co-DFHMA) copolymers with various content of DFHMA, in which the F/C ratio represents the relative magnitude of fluorine concentration at the film surface. It is clear that the F/C ratios for the solvent-borne film are remarkably higher than that for the latex film at any a given DFHMA content. These differences between the solvent-borne film and latex film may be attributed to their film-for-

mation mechanism. During the film-formation of latex, the perfluoroalkyl groups may be embedded in the latex particle. This limits greatly the occupation of perfluoroalkyl groups on the film surface, and thus the efficiency of fluorine is decreased. Furthermore, F/C ratios for the solvent-borne film remain almost constant when the amount of DFHMA in the copolymers exceeds about 5 mol%, whereas for the latex film, 9.5 mol% PDFHMA is needed. These results correspond well with the contact angle results as shown in Figure 4.

As well known, it is of more practical importance to enhance the hydrophobicity and olephobicity of latex film containing fluorine. The contact angle value on the solvent-borne film may be considered as the highest value that the latex film could achieve. The significant surface property gap between the solvent-borne film and latex film provides a potential possibility that the surface property of latex film could be greatly improved. How to improve the surface properties of latex film composed of low level of fluorinated components to the level of the corresponding solvent-borne film will be the focus of the next work.

4. Conclusions

The fluorinated acrylate copolymer, poly (BMA-co-DFHMA), was successfully synthesized by emulsion polymerization using a preemulsified monomer addition process, which was confirmed by FTIR and $^1\text{H-NMR}$. It was found that when the water and oil contact angle reached equilibrium, the required DFHMA content for the solvent-borne film was much lower than that for the latex film. The F/C ratios on the two types of films showed a similar changing trend with the increase of the fluorinated component content. Furthermore, the solvent-borne film, especially at the low level of fluorinated component content, exhibited much more excellent water and oil repellency than the latex film.

The significant surface property gap between the solvent-borne film and latex film indicates that the surface property of the latex film containing lower content of fluorinated components could be further improved to a great degree, which is very important for the practical application of fluorinated acrylate copolymer latex.

Figure 5. F/C ratios at the surface of a series of poly (BMA-co-DFHMA) copolymers with different amount of PDFHMA

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References

- [1] Hochart F., De Jaeger D., Levalois-Grutzmacher J.: Graft-polymerization of a hydrophobic monomer onto PAN textile by low-pressure plasma treatments. *Surface & Coatings Technology*, **165**, 201–210 (2003).
- [2] Yang S., Wang J. G., Ogino K., Valiyaveetil S., Ober C. K.: Low-surface-energy fluoromethacrylate block copolymers with patternable elements. *Chemistry of Materials*, **12**, 33–40 (2000).
- [3] Benedetti E., D'alessio A., Zini M. F., Bramanti E., Tirelli N., Vergamini P., Moggi G.: Characterization of acrylic resins and fluoroelastomer blends as potential materials in stone protection. *Polymer International*, **49**, 888–892 (2000).
- [4] Gu G., Zhang Z., Dang H., Wu Z.: Preparation of hydrophobic thin films based on PTFE/acrylic resin/SiO₂ complex. *Journal of Materials Science*, **39**, 5613–5615 (2004).
- [5] Dreher W. R., Singh A., Urban M. W.: Effect of per-fluoroalkyl chain length on synthesis and film formation of fluorine-containing colloidal dispersions. *Macromolecules*, **38**, 4666–4672 (2005).
- [6] Ha J-W., Park I. J., Lee S-B.: Hydrophobicity and sliding behavior of liquid droplets on the fluorinated latex films. *Macromolecules*, **38**, 736–744 (2005).
- [7] Sacanna S., Koenderink G. H., Philipse A. P.: Microemulsion synthesis of fluorinated latex spheres. *Langmuir*, **20**, 8398–8400 (2004).
- [8] Chen Y., Cheng S., Wang Y., Zhang C.: Chemical components and properties of core-shell acrylate latex containing fluorine in the shell and their films. *Journal of Applied Polymer Science*, **99**, 107–114 (2006).
- [9] Dreher W. R., Jarrett W. L., Urban M. W.: Stable non-spherical fluorine-containing colloidal dispersions: Synthesis and film formation. *Macromolecules*, **38**, 2205–2212 (2005).
- [10] Yang M-J., Zhang W.: Preparation and properties of silicone-acrylate copolymer latex. *Chinese Journal of Polymer Science*, **22**, 215–218 (2004).
- [11] Sharma A., Thampi S. P., Suggala S. V., Bhattacharya P. K.: Pervaporation from a dense membrane: Roles of permeant-membrane interactions, Kelvin effect, and membrane swelling. *Langmuir*, **20**, 4708–4714 (2004).
- [12] Li K., Wu P., Han Z.: Preparation and surface properties of fluorine-containing diblock copolymers. *Polymer*, **43**, 4079–4086 (2002).