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Studies on waterborne polyurethanes based on new medium length fluorinated diols

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ABSTRACT

A novel fluorinated diol 3-(bis-(*N*,*N*-dihydroxyethyl)) dodecafluoroheptyl acrylate (DEFA) was for the first time synthesized via Michael addition reaction between diethanolamine and dodecafluoroheptyl acrylate, followed by a series of waterborne fluorinated polyurethane emulsions IPDI-DEFA-PU synthesis using isophorone diisocyanate (IPDI), poly(tetramethylene oxide glycol) (PTMG), dimethylolpropionic acid (DMPA) and 1,4-butanediol (BDO) as main starting materials, and DEFA as a chain extender. The structure of DEFA and IPDI-DEFA-PU was confirmed by Fourier transform infrared (FTIR) spectroscopy and proton nuclear magnetic resonance (^{1}H NMR). It was found that the fluorine content increased from 0 to 15.1%, and the particle size of emulsion increased from 102 nm to 260 nm, whereas the surface tension of latex film decreased from 42.9 mN/m to 16.5 mN/m; while the water contact angle increased from 71° to 104°, the swelling ratio of latex film in water and cyclohexane decreased from 15.8% to 1.1% and from 28.8% to 3.4%, respectively. Meanwhile, water/organic solvent resistance and thermal stability, mechanical properties of IPDI-DEFA-PU were all improved. As tensile strength increased from 9 MPa to 15 MPa, extensibility decreased from 520% to 280%.

1. Introduction

In recent years, waterborne polyurethane (WPU) has been widely used in leather, adhesive, plastic, textile, water-based ink, water-based wood coatings, external and industrial coating industry due to its good cohesiveness, filming property, abrasion resistance, low temperature resistance and other physical mechanical properties, as well as its good performance against the properties of incombustibility, non-toxicity and less pollution to the environment. The research and development work is focused mainly on WPU containing anionic hydrophilic groups, especially those into which dimethylolpropionic acid (DMPA) or dimethylol butanic acid (DMBA) is introduced. The anionic polyurethane aqueous dispersions are usually obtained by self-emulsification in water after being neutralized with tertiary amine. However, the hydrophilic nature of ionic groups or water-soluble segments of waterborne type polyurethanes inevitably poses some problems associated with poor water resistance and solvent resistance, and bad mechanical properties. In order to improve the shortcoming, some strong hydrophobic groups especially fluorocarbon segment, are commonly introduced into the molecular chain. The modified waterborne fluorinated polyurethane combines some of the virtues of WPU and fluorinated polymer, such as high thermal stability, good chemical resistance, low water absorptivity (water resistance), attractive surface properties, excellent flexibility, good wearability, and high weatherability [1–4].

So far, the general method of introducing fluorocarbon segment mainly focused on using small molecule containing fluorine and fluorinated macromolecular glycol as a chain extender, blocking fluorine chemically into polyurethane (PU) chain [5–12], or forming hybrid emulsion using polymerized fluorine-containing acrylate with polyurethane [13–20]. These methods generally embedded fluorine atoms into molecular main chain. During the formation of latex film, the migration quantity of fluorine to the film surface does not work well because the movement of fluorine-containing segments with low surface energy is restricted by the movement of full molecular chains. In WPU systems, too longer hydrophobic segments will interfere with the mobility and the liquid character of the micro-phases, whereas too shorter segments will interfere with the hydrophobic phase separation from the aqueous phase [21]. Also, the main disadvantage of a fluorinated monomer is its relatively high cost. Therefore, the

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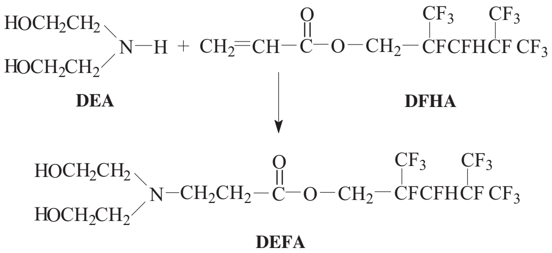

Scheme 1. Synthesis of DEFA.

content of fluorinated monomers should be minimized while the low value of surface tension was obtained (water/oil repellency).

In view of these problems, the synthesis of a novel fluorinated diol 3-(bis-(*N*,*N*-dihydroxyethyl)) dodecafluoroheptyl acrylate (DEFA) by using diethanolamine and dodecafluoroheptyl acrylate was carried out. This was followed by the preparation of a polyurethane aqueous emulsion IPDI-DEFA-PU with fluorinated medium branched chain using DEFA as a chain extender. Based on the measurement and analysis of the surface tension, contact angle with water, the swelling ratio in water/cyclohexane and stress–strain curve for the latex film, different contents of fluorinated moieties in IPDI-DEFA-PU with relevant performances was systematically investigated. By choosing suitable techniques and appropriate fluorine content, the stable IPDI-DEFA-PU aqueous emulsion and the latex film with low surface tension can be successfully prepared.

2. Results and discussion

2.1. Structure analysis using FTIR and ^{1}H NMR

As shown in Scheme 1, the double bond in DFHA will gradually disappear as the reaction progresses and DEFA is formed. In order to understand the generation of DEFA during its synthesis, infrared spectroscopy was used to monitor the reaction process. FTIR spectra monitor the range between 1550 and 1850 cm^{-1} for the mixtures of DEA, DFHA and DEFA at different reaction times (Fig. 1). The absorption peak located at 1734 cm^{-1} is attributed to stretching vibration of the ester carbonyl bond (C═O), while that located at 1640 cm^{-1} can be attributed to the stretching vibration of the alkene bond (C═C). Fig. 1 shows that the peak at 1640 cm^{-1} gradually decreased with the increase of reaction time. This suggested that an addition reaction between the NH group of DEA and the C═C of DFHA occurred, hence suggesting that DEFA was generated. For the absorption peak of 1734 cm^{-1}, the peak symmetry gradually changed and peak location moved to a higher wavenumber. A blue shift of 24 cm^{-1} from 1734 cm^{-1} to 1758 cm^{-1} was observed at the end of the reaction. The phenomena of a blue shift can be attributed to the reduction of the C═C group and the break of the conjugate system in DFHA with the addition reaction, which also proves that the amount of DEFA increases gradually with the increase of reaction time. As can be seen from the infrared spectra (Fig. 1), the reaction goes to completion within 8 h.

The molecular structure of DEFA can be further confirmed by ^{1}H NMR spectroscopy (Fig. 2). Peak *a* located at 2.28 ppm is contributed by the proton of methylene connected to carbonyl group, peak *b* located at 2.62 ppm is produced by the proton of methylene connected with nitrogen, and peak *c* located at 3.63 ppm is attributed to the proton of methylene connected to hydroxyl group. Due to the coupling effect of the adjacent methylene proton, it appeared as a triplet peak. Peak *d* located at 3.88 ppm only appears as unimodal form, contributed by the proton of hydroxyl group as there is no adjacent proton coupling effect. Peak *e* was located between 4.65 and 4.80 ppm and was assigned to the protons of –CFCH$_2$O– group, it appears as multiple peaks because of common coupling effect between α and β fluorine atoms. A slight difference with the other peak is the appearance of *f*, which is contributed by the proton of –CFH. Due to the coupling action of adjacent fluorine atoms connected to –CFCF$_3$ and –CF(CF$_3$)$_2$, all bimodal appeared as multiple peak between 4.89 and 5.09 ppm. The ^{1}H NMR spectral analyses demonstrated that the ratio of integrated values of peaks was 2:6:4:1.5:0.7, approximately 2:6:4:2:1, which revealed the presence of 2, 6, 4, 2 and 1 protons at chemical shifts 2.28, 2.62, 3.63, 4.65–4.80 and 4.89–5.09 respectively.

2.2. Chain structure analysis of IPDI-DEFA-PU by FTIR

The chain structure of IPDI-DEFA-PU was confirmed by FTIR spectroscopy. FTIR spectra of DEFA-PU0 and DEFA-PU5 are shown in Fig. 3. Whether samples contained fluorine or not, the typical absorption peaks of polyurethane are observed at 3329 cm^{-1} [ν(NH)], 2863–2943 cm^{-1} [ν(CH$_2$) and ν(CH$_3$)], 1710 cm^{-1} [ν(C═O)], 1532 cm^{-1} [δ(N–H)], 1108 cm^{-1} [ν(C–O–C)] and 1236 cm^{-1} [ν(CN)] in both spectra. The peak at 1236 cm^{-1} of DEFA-PU5 is overlapped by the strong peak located at 1193 cm^{-1} [ν(CF)]. In addition, absorptions at 1282 cm^{-1} and 1193 cm^{-1} can be assigned to the stretching vibration of C–F bonds in polyurethane chains of DEFA-PU5. Moreover, the peak located at 836 cm^{-1} was assigned to the characteristic absorption peak of the CF$_3$ group. The appearance of three peaks indicated that the structure of DEFA as a chain extender has been incorporated into the molecular chain of IPDI-DEFA-PU. The absorbance peaks disappear gradually at around 2260 cm^{-1} (NCO), which indicates that all the NCO groups of the isocyanate were reacted. These changes in peak observation indicate that IPDI-DEFA-PU with fluorinated medium branched chain is synthesized successfully.

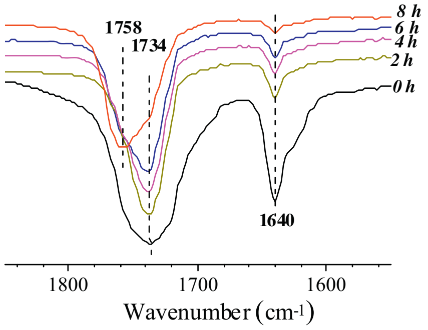

Fig. 1. FTIR spectra of DEFA at different reaction times.

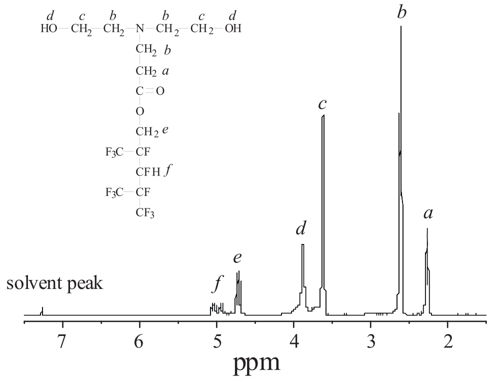

Fig. 2. ^{1}H NMR spectrum of DEFA.