

Synthesis and Characterization of Novel Fluorine-Containing Water-Based Antirust Coating

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Abstract. A fluorine-containing polyacrylate copolymer emulsion was synthesized by a seed emulsion polymerization method, in which styrene(St) and butyl acrylate (BA) were used as main monomers and dodecafluoroheptyl methacrylate(DFMA) as fluorine-containing monomer. The structure and properties were characterized by Fourier transform infrared spectrum (FT-IR), scanning electron microscopy (SEM), particle size analysis, differential scanning calorimetry (DSC). The FTIR results showed that DFMA was effectively involved in the emulsion copolymerization, and the formed emulsion particles had a narrow particle size distribution. From the results salt spray test presented, it seems when the content of DFMA was 5wt% anti-rust performance of emulsion is relatively better. DSC and TGA also showed that their film exhibited higher thermal stability than that of fluorine-free emulsion.

1. Introduction

Owing to the low polarizability and strong electronegativity of the fluorine atom [1], fluorinated polymers have many useful and desirable features [2] such as, excellent thermostability and antichemical properties[3,4], low levels in surface energy and flammability [5,6]. However, the relatively high market price of fluorinated monomers limits their use [7], thus, the fluoromonomer and its polymers are often used as modifiers.

Acrylic resin, prepared through the polymerization of acrylic, methacrylic acid esters and other olefinic monomer, exhibits advantages such as high adhesion, high resistance to heat, corrosion and stain; as well as comparatively low price [8, 9]. Yet, it also has distinct disadvantages in the coating compactness and the shielding properties for steam and flash-rust [10] due to its intrinsic chemical properties, ultimately limiting its application [11]

Introducing fluorine-containing group is a way to change the structure of acrylate copolymer, which can maintain the original excellences of acrylate copolymer and obtaining the hydrophobic, oil-repellency and durability of fluorocarbon polymer at the same time [12]. Therefore, fluorine-containing acrylate emulsion has become a kind of coatings with good comprehensive performance and wide application prospects[13]. In this paper, the fluorinated acrylate copolymer emulsion with core-shell structure was synthesized by a seed emulsion polymerization method, in which styrene and butyl acrylate (BA) were used as main monomers and dodecafluoroheptyl methacrylate (DFMA) as fluorine-containing monomer. The results showed that DFMA effectively involved in the emulsion copolymerization, the content of DFMA has a great influence on the properties of the emulsion.



2. Experimental

2.1. Materials

Styrene (St), butyl acrylate (BA) and acrylic acid (AA) was purified by distillation under vacuum before using. Dodecafluoroheptyl methacrylate (DFMA) was obtained from Zhengzhou Alpha Chemical Co., Ltd., and used as received. Sodium dodecyl sulfonate (SDS), and nonylphenol polyoxyethylene ether (OP-10), as emulsifier, were used without further purification. N-Methylolacrylamide (N-MA), sodium dihydrogen phosphate and potassium persulfate, respectively used as crosslinking agent, buffering reagents and initiator, were used as received.

2.2. Synthesis of Fluorine-Containing Polyacrylate Emulsion

In this paper, the author adopted pre-emulsion polymerization process to synthesis fluorine-containing polyacrylate emulsion. And the synthesis procedures utilized can be described as follows.

First, SDS, OP-10 and some deionized water were prepared as emulsifier mixture through stirring. At meantime, St, BA and quantitative DFMA were mixed as monomer part. The mixture of functional monomer involved N-MA, AA, and deionized water. Sodium dihydrogen phosphate and potassium persulfate were dissolved in deionized water, the initiator-buffer solution was prepared

Secondly, a part monomer, half of emulsifier mixture, all functional monomer and an appropriate amount of deionized water reacted for 30min under vigorous stirring. Gradually, the mixture become white, pre-emulsion was formed.

A certain amount of deionized water, the remaining emulsifier, as well as another monomer were added into the flask. Initiator-buffer solution was added dropwise to the above mixture. This solution was then heated to 70°C with stirring. When the emulsion produces blue light, started to drop the prepared pre-emulsion and the rest initiator-buffer solution, lasted for about 3 hours. The reaction temperature was heated up to 80°C when it was finished, and then the reaction continued for another 2h under this condition.

Finally, filtered and discharged.

2.3. Characterization

FT-IR spectra were collected on a Nicolet IS5 Fourier transform infrared spectrometer (Nicolet Instruments Co., USA) in the range from 400 to 4000cm⁻¹. The particle size and its distribution of synthesized emulsion were measured by laser particle size distribution instrument (Dandong Baxter Instrument Co., Ltd). The scanning electron microscopy (SEM) micrographs were obtained by using S-4800 scanning electron microscope (HITACHI Company Ltd, Japan). The glass transitions temperature (T_g) of co-polymer was measured by FC100 differential scanning calorimetry (TA Instruments Co., USA).

3. Results and Discussion

3.1. FT-IR Analysis

Figure 1 illustrates the FT-IR spectra of emulsion film. The absorption band at 2927 and 2873cm⁻¹ represent the C-H stretching vibration, and the absorption band at ~1726cm⁻¹ is attributable to the carbonyl (C=O) stretching vibration. Furthermore, the bands occurring at 1155 and 1157cm⁻¹ assign to the ester groups (-COO-). Compared with Figure 1(a), the band at 697cm⁻¹ represents the C-F stretching vibration, and the absorption peak between 1064-1451cm⁻¹ is significantly wider, which is the result of the superposition of C-O, C-C and C-F bonds. The above description showed the presence of fluorine-containing groups in the polymer, i.e., the fluorine-containing monomer DFHM effectively participates in the copolymerization reaction.

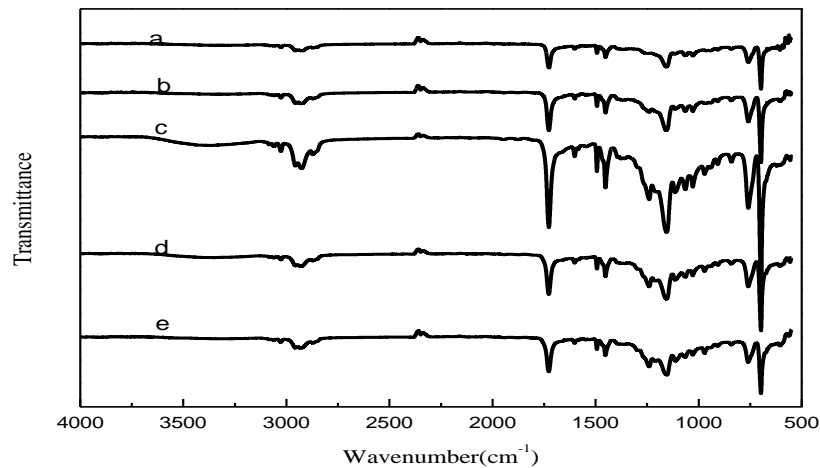


Figure 1. FT-IR spectra of the emulsion film--SDS/OP-10 as emulsifier a-DFMA 0%; b-DFMA 5%; c-DFMA 10%; d-DFMA 15%; e-DFMA 20%

3.2. Particle Size, Distribution and Morphology

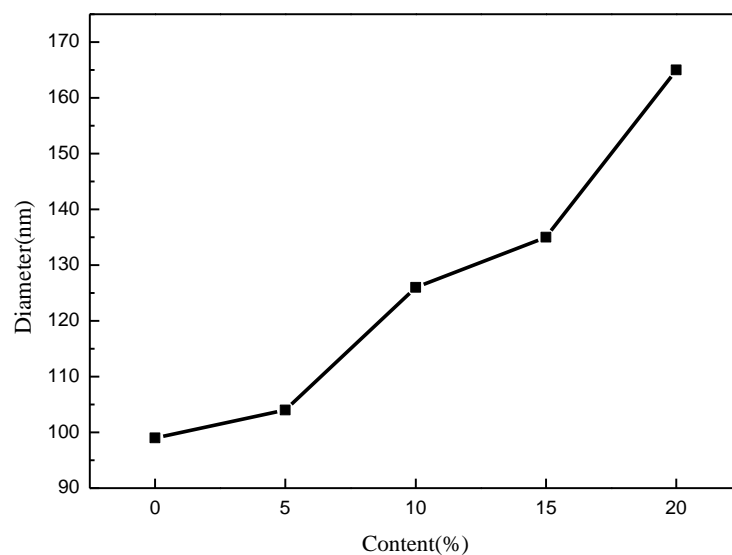
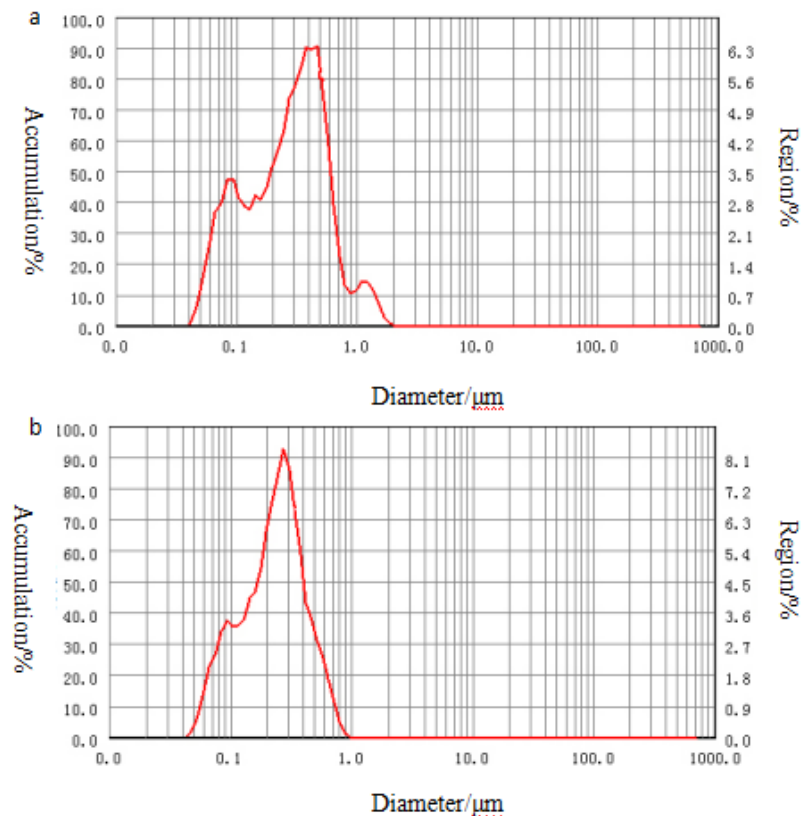
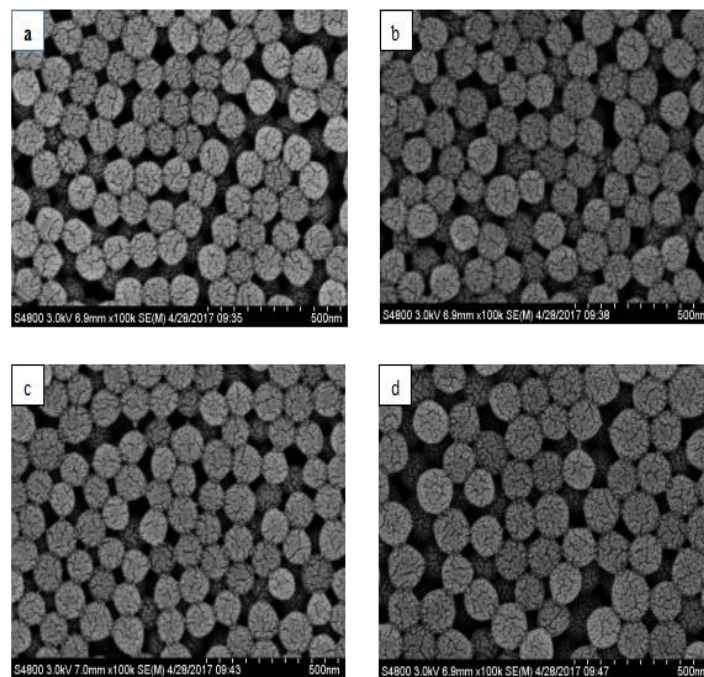


Figure 2. Particle size diagram of latex with different DFHM content



a-the fluorine-free polyacrylate emulsion; b-the fluorine-containing polyacrylate emulsion
Figure 3. Emulsion particle size distribution diagram



a-d: the content of DFMA was 5%, 10%, 15% and 20%, respectively, and they all use SDS / OP-10 as emulsifier

Figure 4. SEM micrograph of polyacrylate emulsion particles

In the process of emulsion synthesis, the distribution and size of latex particles have great influence on the appearance, film forming performance and physicochemical properties of emulsion film. Figure 2 is particle size diagram of latex with different DFHM content. As can be seen from the curve, with the concentration of DFHM monomer increases, the diameter of latex particles increases. From the result presented here, it seems that with the increase of the amount of fluorinated monomer, the hydrophobicity become too strong, which destroys the hydrophilic and lipophilic balance of emulsifiers, then leads to the decrease of the stability of latex particles. Therefore, DFHM will increase the particle size of the emulsion.

From the Figure 3, emulsion size distribution diagram, the fluorine-free acrylate emulsion has a wide particle size distribution, whereas the size distribution of the emulsion is narrowed by the addition of fluorine-containing monomers, and narrow distribution indicates that the size of latex particles is more uniform and the structure is also stable. That is, fluorinated monomer DFMA is added to make the performance of emulsion better. On the other hand, hydrophilic AA provides the necessary conditions for the stability of hydrophobic monomers BA and DFHM to some extent.

Figure 4 illustrates SEM micrographs of the polyacrylate emulsion film with different content of DFMA. The SEM image in Fig.4 show that the morphology of prepared colloidal particles is regular, the appearance of the particles is spherical, in addition, the particle size distribution is uniform.

3.3. Salt Resistance Analysis

Table 1. The effect of fluorine-containing monomer on the salt spray resistance of the coating

DFMA Time/h	24h	36h	48h	72h
0	#	##	##	###
5	#	#	#	##
10	#	#	#	###
15	#	#	##	###
20	#	##	##	###

Note: #-Substrate no rust point ##-The substrate appears part of the rust point ###-Substrate appears small area rust point

As can be seen from Table 1, with the increase in the amount of fluorine-containing monomer DFMA, the anti-rust performance of the emulsion is enhanced. The acrylate emulsion, which does not contain the DFMA monomer, begins to show a rust point after putting in the salt spray machine for 24 h, and the fluorine-containing acrylate emulsion does not appear to have a rust point, which may relate to the hydrophobicity of the fluorine-containing monomer, who strengthen the ability of anti-rust. However, the anti-rust ability of the emulsion did not increase with the increase of the content of DFMA monomer, in the subsequent 36h to 72h. From this phenomenon we may come to the conclusion that when the DFMA content is 5%, the anti-rust ability of the emulsion is the best. This is because, when the concentration of DFMA monomer is too high, the strong hydrophobic ability makes it difficult for DFMA to enter the latex particles. The formation of copolymer emulsion is difficult; on the contrary, it reduces the anti-rust ability of emulsion.

3.4. Thermal Analysis

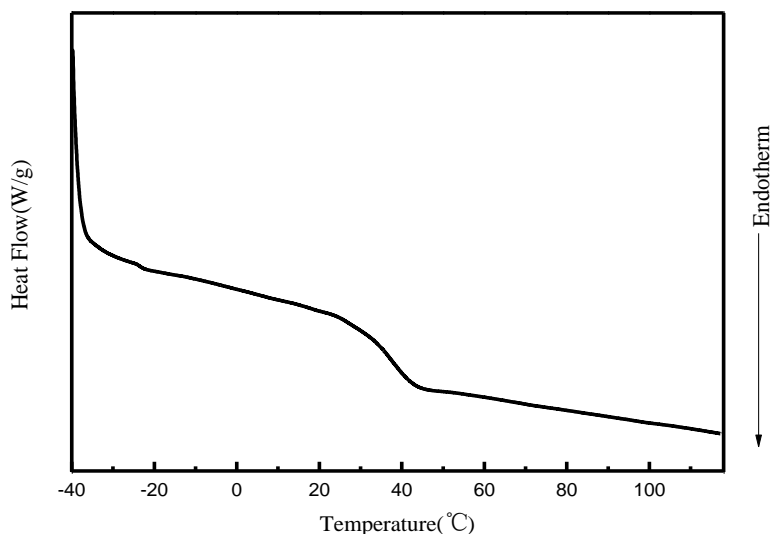


Figure 5. The DSC curve of emulsion film

The typical DSC thermograms of fluorine-containing polyacrylate emulsion film were shown in Figure 5. It can be seen that the T_g of the film was 37.61 °C, close to room temperature, therefore, it is reasonable to have relatively lower minimum film forming temperature, and it is easy to operate at low temperatures. But low glass transition temperature will make the coating soft, and easy to stain.

4. Conclusions

A type of waterborne fluorine-containing polyacrylate emulsion was successfully synthesized using a mixture emulsifier system via an emulsion polymerization approach. The results of FT-IR showed that DFMA was effectively involved in the copolymerization, and particle analysis suggested that emulsion particles were uniform in size and narrow in particle size distributions (PSD) when the content of DFMA was 5wt%. SEM, DSC and TG analysis indicated that the synthesized fluorine-containing polyacrylate emulsion particles distributed evenly, and that the copolymer film showed higher thermal stability. From the results salt spray test presented, it seems when the content of DFMA was 5wt%, anti-rust performance of emulsion is relatively better, and the application prospect is very broad.

5. References

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