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Effect of ionic liquids on stability of O/W miniemulsion for application of low emission coating products[☆]

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ABSTRACT

Room temperature ionic liquids (RTILs) are non-volatile organic salts. They may replace conventional coalescing agents in latex coating thus reducing volatile organic compounds (VOCs) emission as well as improving performance of latex coating products such as better thermal stability, conductivity, and antifouling property. The formation of latex coating containing RTILs can be achieved by encapsulation of RTILs inside particles *via* miniemulsion polymerization. In this study, the role of RTILs and its concentration on stability of miniemulsion during storage and polymerization were investigated. It has been found that, above a critical concentration (10 wt%), adding more RTILs to oil phase may weaken miniemulsion stability during storage as well as polymerization. Such observations were consistent with the zeta potential measurement for miniemulsions prepared at the similar conditions. The results obtained here would be a useful guideline for the development of new waterborne coating products with desirable functions and particle sizes.

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1. Introduction

As legislations against volatile organic components (VOCs) become more stringent, there has been a trend towards waterborne coating. Among waterborne coatings, latex coating, prepared by mixing latex with fillers, pigments, and additives, has attracted increasing attention [1]. It is widely applied in architectural field, including interior coating, exterior coating, and wood paint. However, VOC emission from coalescing agent is a main challenge of latex coating. Coalescing agent can be classified as a plasticizer that reduces the glass transition temperature (T_g) of polymer. It functions as enhancing the deformation and coalescence of particles, which is essential for forming a continuous film. But after film formation coalescing agent diffuses and evaporates as VOCs. Some of them, for example, the well-known Texanol, even release a weak and unpleasant odor persisting for days [2].

It is notable that some of the room temperature ionic liquids (RTILs), kinds of non-volatile organic salts, are proven to be effective plasticizers to reduce T_g of polymers [3,4]. Due to plasticizer effect and non-volatility, RTILs may act the same as coalescing agents, but eliminate the emission of VOCs. After film formation, RTILs remain in the film as polymer/RTILs composite, and provide the film with some special functions like thermal stability, conductivity, and antifouling property [5–9]. It can be seen that a certain RTIL may have the potential to be a

coalescing agent with multi-function and minimum VOC emission, which coincides with the development tendency of additives for latex coating.

The method of adding RTILs into latex coating is worth considering. To improve water resistance of film, RTILs must be hydrophobic; and hydrophobic RTILs cannot be dispersed in water phase directly. Encapsulation of RTILs inside polymer particles by miniemulsion polymerization is a good choice. In miniemulsion polymerization, polymerization carries out primarily according to droplet nucleation mechanism, where monomers are polymerized directly inside droplets [10]. Because the final particles originate from droplets, hydrophobic compounds presented in droplets would be gradually encapsulated by polymers formed till the end of polymerization. Some hydrophobic compounds like Miglyol 812, castor oil, and *n*-heptane [11–13], have been successfully encapsulated by this method. This indicates the potential to encapsulate RTILs by miniemulsion polymerization.

To prepare homogeneous latex containing RTILs, the stability of miniemulsion should be concerned. Such stability includes the storage period before polymerization. This would further affect the stability of miniemulsion during polymerization [10]. During storage, the instability of miniemulsion can be classified into two types: reversible and irreversible change [14]. For reversible change, droplets first flocculate, followed by creaming or sedimentation. Irreversible change includes coalescence and Ostwald ripening, thus leading to the formation of larger droplets. Ostwald ripening is a phenomenon that describes the diffusion of monomer from small droplet into large droplet caused by the higher interfacial energy of small droplet than that of large one. Coalescence is the process of formation of larger droplet caused by the collision of smaller droplets. The unstable phenomenon of miniemulsion

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observed during polymerization has some similarity to the one observed during storage. Oil phase may separate from miniemulsion at the early stage of polymerization. Miniemulsion could become viscous followed by the coagulation of particles which would separate from miniemulsion at the end of polymerization. Sometimes products are stable and homogeneous based on direct observation, however, under the observation *via* microscope, the particles could be bridged together [15].

So far, no report has been published on relations between RTILs and stability of miniemulsion during storage as well as during the polymerization process. Our work will focus on the investigation on the effect of RTILs on stability of miniemulsion before and during polymerization. 1-Octyl-3-methyl-imidazolium hexafluorophosphate (C_8mimPF_6) is chosen as the target RTIL. Reasons have been explained elsewhere [16].

2. Materials and Methods

2.1. Chemicals

Methyl methacrylate (MMA, CP) was purchased from Sinopharm Chemical Reagent Co., Ltd and purified by vacuum distillation to remove inhibitor. L-Ascorbic acid (Vc, AR), hydrogen peroxide (H_2O_2 , AR), and sodium dodecyl sulfonate (SDSO, CP) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hexadecane (HD, 98%) was purchased from Aladdin Industrial Inc. 1-Octyl-3-methylimidazolium hexafluorophosphate (C_8mimPF_6 , 99%) was supplied by Shanghai Cheng Jie Chemical Co., Ltd. Ultra-pure water with a resistivity of $18.2 M\Omega \cdot cm^{-1}$ was used in all experiments.

2.2. Preparation of miniemulsion

Oil in water miniemulsion (O/W) was prepared with a volume ratio of oil to water phase equal to 3 to 7. The oil phase contained 5 wt% HD, the remaining 95 wt% containing C_8mimPF_6 and MMA. Both C_8mimPF_6 and HD were infinitely miscible in MMA. The water phase contained $30 mmol \cdot L^{-1}$ SDSO. After HD and C_8mimPF_6 were fully dissolved into MMA, the oil phase was added into water phase in a 100 ml plastic container and kept at 40 °C. Ultrasound probe was then placed 1 cm below the surface of the mixture in the middle of the container. The output power of the sonicator (Xinzhi Scientz II) was set as 95 W. The miniemulsion was formed by homogenizing the mixture for 6 min in a state of 1 s on and 1 s off.

2.3. Miniemulsion polymerization

The polymerization was carried out in a 250 ml four-necked flask equipped with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet. The flask was immersed in a water bath for controlling reaction temperature. 150 ml miniemulsion was loaded into the flask, and stored under stirring and nitrogen bubbling for 1.5 h to remove oxygen. Then set the temperature of water bath to the reaction temperature. After the desired reaction temperature, 40 °C, was reached, adding initiator solution, $H_2O_2 + Vc$, into water phase to start polymerization reaction. The initiator solution was prepared by dissolving a given amount of Vc in 5 ml ultra-pure water, then adding H_2O_2 in to Vc solution. The molar ratio of H_2O_2 to Vc equal to 1 to 1.3. In this work, 1 mol% of H_2O_2 based in MMA is used.

2.4. Characterization

2.4.1. Stability of miniemulsion

Miniemulsion was visually observed during storage and polymerization to evaluate if any creaming, sedimentation, phase separation, and coagulation occurred.

2.4.2. Droplet size measurement

The droplet/particle sizes and distributions of miniemulsion at different storage/reaction times were measured using the laser diffraction method (Mastersizer 3000, Malvern Inc). This technique has been widely accepted as a tool to evaluate droplet size [17–19]. Before the size measurement, the sample was diluted with water solution to meet the requirement of obscuration. The diluted water solution was saturated with SDSO and monomers to prevent coalescence during sample measurement [20]. All measurements were repeated three times.

2.4.3. Interfacial tension measurement

The interfacial tension between oil phase and water phase was measured using the Du Noüy ring method (BZY-2tensiometer, Hengping Instruments). Since above a certain concentration, the surfactant (SDSO) cannot be dissolved in water phase at the storage temperature, 20 °C, the measuring temperature was set at 40 °C. Measurements were repeated three times.

2.4.4. Zeta potential measurement

The Zeta potentials of the miniemulsion were measured using trace laser Doppler electrophoresis method (Zetasizer Nano ZS, Malvern Inc) at 20 °C. Measurements were carried out by injecting the miniemulsion sample into high concentration sample cell and it was repeated three times.

2.4.5. Determination of conversion

The conversion of monomer was determined gravimetrically. The product was sampled at regular intervals during reaction, and stored in refrigerator immediately after being taken out to terminate the reaction. After evaporating monomer under ventilated condition and storing in an oven at 120 °C for 4 h, polymer, C_8mimPF_6 , and SDSO remained in the solid product. Because the content of C_8mimPF_6 and SDSO can be calculated according to raw material ratio, the yield of polymer can be obtained by subtracting the content of C_8mimPF_6 and SDSO from the solid product.

3. Results and Discussion

In this section, effect of C_8mimPF_6 concentration on stability of miniemulsion during storage and polymerization, was systematically investigated.

3.1. Effect of C_8mimPF_6 concentration on stability of miniemulsion during storage

In order to evaluate the role of C_8mimPF_6 on stability of miniemulsion during storage, miniemulsions containing different concentrations of C_8mimPF_6 ranging from 0 wt%, 1 wt%, 5 wt%, 10 wt%, 20 wt% to 30 wt% based on oil phase were prepared, and were stored at 20 °C for 288 h. Results were listed in Table 1.

Table 1

Droplet sizes of miniemulsions containing different concentrations of C_8mimPF_6 before and after 288 h storage

C_8mimPF_6 mass content/%	Initial droplet size/nm	Droplet size after storage/nm	Increase rate of droplet size/%	Creaming or sedimentation
0	245	268	9.4	No
1	228	233	2.2	
5	228	236	3.5	
10	235	272	15.7	
20	270	325	20.4	
30	280	411	46.8	

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