Application of Diacetone Acrylamide and Adipic Dihydrazide in Epoxy-acrylate Self-crosslinking Latex

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Abstract: The DAAM is used as the functional monomer, and the epoxy-acrylate latex which contains ketone carbonyl is prepared. The latex is mixed with ADH (adipic dihydrazide) and the self-crosslingking latex is prepared. The FTIR and TEM for the film curing are analyzed, test results prove that the reaction between ketone carbonyl and hydrazine has happened during the film curing, and the best condition is in alkaline and weak acid.
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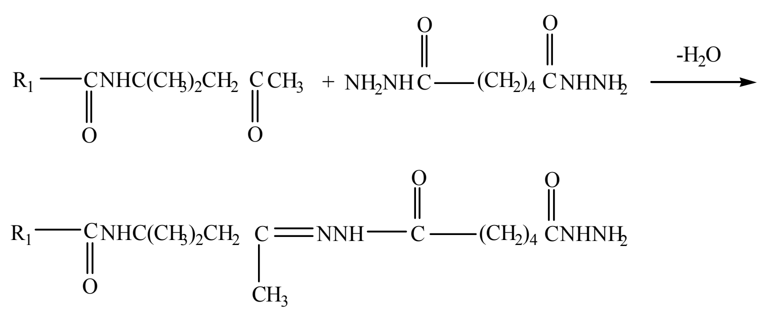
Key worlds: DAAM, ADH, self-crosslinking.

1. Introduction

First introduce ketone carbonyl to the macromolecular polymer chain in waterborne polymer latex, and then taking hydrazide as the crosslingking agent to achieve the room temperature crosslingking for latex has become the hotspot issue for the worldwide research in recent years. The monomer that can introduce ketone carbonyl to macromolecular polymer chain are Diacetone acrylamide (DAAM), methylacrolein and methyl vinyl ketone (Jiang S J,2003). DAAM is the basic functional monomer to introduce ketone carbonyl to acrylate macromolecular polymer chain. It is not only because the material to synthesize DAAM is simple, but also because DAAM has low toxicity, and DAAM can reinforce the cohesion capability of coating. When the adipic dihydrazide (ADH) is applied to the latex which contains ketone carbonyl, the reaction between ketone carbonyl and hydrazine will happen in the acid condition after the latex has forming film (Nicola et al., 2008). As a result the latex polymer can achieve room temperature crosslingking (Chi L, 2004).

The reaction between ketone carbonyl and hydrazine is shown bellow (Liu YP et al., 2006):



2. Material and Methods

2.1 Preparation of auto-crosslingking epoxy-acrylate latex contains ketone carbonyl

(1) Preparation of epoxy-acrylate latex contains DAAM (It is denoted by P (EP-A$_i$), and i is the DAAM percentage to the monomer gross)

The SDS, OP-10, BA, St, MMA and deionized water are first stirred at high speed to prepare acrylate preemulsified monomer and 30% of the monomer mixture is added into a 500ml flask at 60℃and heated to 75℃ for 1h to obtain the seed latex. This is followed by the addition of the remnant preemulsified monomer. The remnant preemulsified monomer after adding MAA is named as monomer (a). And monomer (b) is prepared by adding DAAM into 30% monomer (a). The dropping sequence is first monomer (a) and then monomer (b) and epoxy resin finally. After adding all the ingredients, the reaction mixture was heated for an additional 1.5h to complete the reaction of the residual monomers to obtain the composite latex.

(2) Preparation of latex with different DAAM and ADH ratio (It is denoted by P (EP-Ai) J (x:y), and P (EP-Ai) is the number of epoxy-acrylate, i is the DAAM percentage to the monomer gross, (x:y) is the mol ratio of ketone carbonyl to hydrazine)

The 10% ADH solution is added into P ($EP-A_6$) latex and stirred at room temperature for 15min and the pH is adjusted to 9-10 and mole ratio of ketone carbonyl to hydrazine is 2:1 and 1:1. The number for latex without hydrazine and with hydrazine are denoted as P ($EP-A_6$) $J_{0,}$ P ($EP-A_6$) J $_{(2:1)}$ and P ($EP-A_6$)J $_{(1:1)}$, respectively.

2.2 Characterization

The FTIR spectra were obtained using a Fourier transform infrared spectrometer (Ncolet Instruments, 60sXB). The scanning range is 500-4500 cm^{-1}. The latex is cast on clean glass and dried to prepare film for FTIR analysis.

The morphology of latex particles is examined with a JEOL 100 U transmission electron microscope (TEM). The staining with Phosphotungstic acid (PTA) is carried out as follows. The latex is first diluted to 1000 times and then, the same volume for latex and PTA (3%) solution (pH=1.5) are mixed for 3min. A copper microscope grid is dipped into the mixture, and put on a filter paper, then dries at room temperature.

3 Results and discussion

3.1 Reacting condition exploration for DAAM and ADH

It is reported in the literature (Ma,2003, Xiaohua Liu,2007, Tamaki,2007) that if the ADH is added into the latex for which DAAM has copolymerized and then, pH of composite latex system is adjusted to alkaline with ammonia, the reaction between ketone carbonyl and hydrazine will occur in the acid condition after the ammonia has 挥发 during latex forming film. In order to simulate the curing and confirm the best pH for the reaction of DAAM and ADH, it is necessary to get rid of the latex effect on the crosslinking reaction. DAAM is dissolved with ethanol and ADH is dissolved with deionized water, separately. Then the DAAM solution and ADH solution are first mixed to make the mole ratio of ketone carbonyl to hydrazine be 1:1 and then, the mixture is divided into 8 equivalent parts. pH for 8 equivalent parts are first adjusted to 3, 4, 5, 6, 7, 8, 9, 10 with dilute acid solution and dilute alkali solution respectively and then dried in air seasoning and tested for the FTIR.

It is reported in a lot of literatures (Cui YZ, 2000,2002, Tian-Ying Guo,2007) that hydrazone (C=N) will be formed after the reaction between ketone carbonyl and hydrazine, for which the characteristic absorption peak is about 1665cm^{-1}. The absorption peak intensity for ketone carbonyl (C=O, 1720cm^{-1}) should decrease and absorption peak intensity for hydrazone (C=N, 1660cm^{-1}) should increase along with the DAAM and ADH reaction. However, the methyl absorption peak (CH_3) intensity should be not affected by the reaction in theory. As a result the absorption peak intensity for ketone carbonyl and hydrazone is compared by normalizing the methyl absorption peak of the whole FTIR spectra (see Figure 1). It is indicated in the FTIR peak intensity for pH3~pH10 that the best pH for the reaction is alkaline and weak acid, it go against the reaction for strong acid (pH3~pH4) and neutrality (pH7).

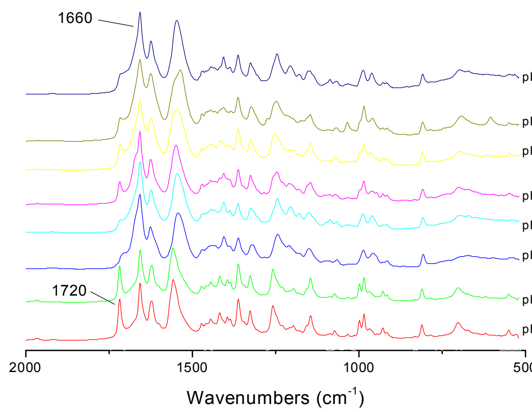


Figure 1. FTIR of system with different pH: pH are 3, 4, 5, 6, 7, 8, 9, 10, respectively

3.2 Simulation for crosslinking reaction

It is indicated in the test result that the best pH for reaction of ketone carbonyl and hydrazine is alkaline and weak acid. In order to simulate the crosslinking course during the ammonia evaporation in the film forming process, the DAAM copolymerized latex is prepared and the pH is adjusted to 7 with $NaHCO_3$ solution. The ADH is added into the pH7 latex to make the mole ratio of ketone carbonyl to hydrazine is 1:1 and then, the latex mixture is divided into 7 equivalent parts. pH for 7 equivalent parts are first adjusted to 3, 5, 6, 7, 8, 10,11 and then, dried in air seasoning and tested for the FTIR.

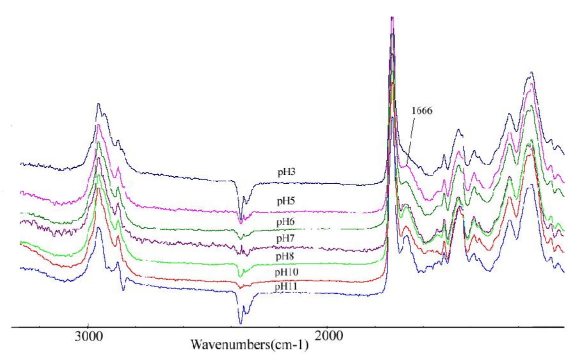


Figure 2. FTIR of latex with different pH: pH are 3, 5, 6, 7, 8, 10, 11, respectively

FTIR for 7 samples are disposed by normalizing the methyl absorption peak to analyze the effect of pH to hydrazone (C=N). It is indicated in Figure 2 that there is no characteristic absorption peak in $1666 cm^{-1}$ when pH is 3. There is the characteristic absorption peak in $1666 cm^{-1}$ when pH is from 5 to 11, for which the characteristic absorption peak intensity of pH7 is comparatively weak. The test result is consistent with the result in 3.1, which further confirms the best reaction condition for ketone carbonyl and hydrazine is in alkaline and weak acid.

3.3 FTIR spectra for latex self-crosslinking

The DAAM copolymerized latex P ($EP-A_6$) is first adjusted to pH9 with ammonia and then, the ADH solution is added into the latex to make the mole ratio of ketone carbonyl to hydrazine is 2:1 and 1:1. The number for latex without hydrazine and with hydrazine are denoted as P ($EP-A_6$)J_0, P ($EP-A_6$)$J_{(2:1)}$ and P ($EP-A_6$)$J_{(1:1)}$, respectively. TFIR spectra for the samples are shown in Figure 3.

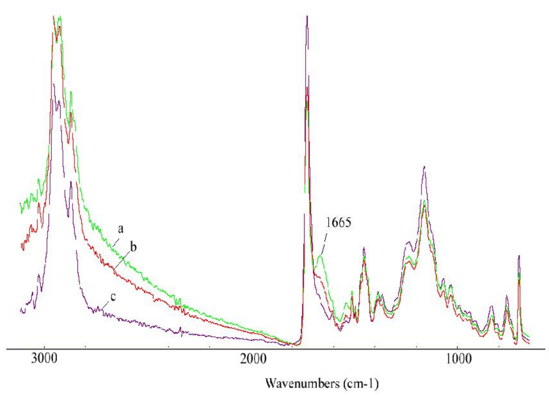
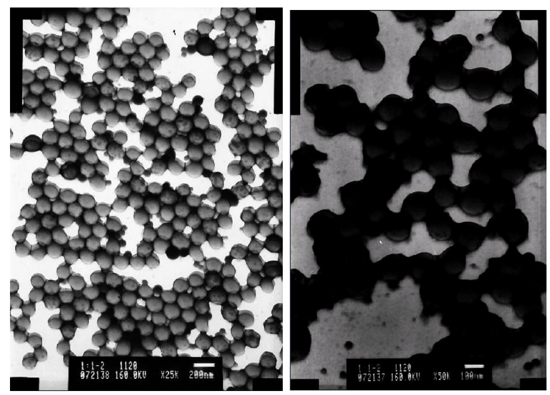


Figure 3. FTIR of latex：A: P ($EP-A_6$) $J_{(1:1)}$; B: P ($EP-A_6$) $J_{(2:1)}$; C: P ($EP-A_6$) J_0

Figure 3 shows the FTIR spectra for latex which mole ratio of ketone carbonyl to hydrazine is 2:1 and 1:1. FTIR of latex without ADH is indicated in Figure 3, too. Characteristic absorption peak for hydrazone is analyzed by comparing the three spectra. There is Characteristic absorption peak at $1665 cm^{-1}$ for both sample P ($EP-A_6$) $J_{(1:1)}$ and sample P ($EP-A_6$) $J_{(2:1)}$, the peak intensity increases along with the increase of ketone carbonyl to hydrazine mole ratio. However, there is no characteristic absorption peak at $1665 cm^{-1}$ for sample without ADH (sample P ($EP-A_6$) J_0). It is obvious that the latex pH can cause the reaction between ketone carbonyl and hydrazine to make the particles crosslink with each other during the latex forming film in air seasoning.

3.4 TEM

Figure 4 shows the TEM micrograph of sample P ($EP-A_6$) J_0 and sample P ($EP-A_6$) $J_{(1:1)}$ stained by pH1.5 PTA. TEM micrograph for latex without ADH (P ($EP-A_6$)J_0) indicates the spherical particles exist independently, which implies there is no chemical crosslinking for epoxy-acrylate latex without ADH. However, TEM micrograph for P ($EP-A_6$)$J_{(1:1)}$ latex indicates spherical particles disappear almost completely, which has merged into each other and joined together. As a result the TEM micrographs prove the reaction between ketone carbonyl and hydrazine results in the crosslingking of particles.



(a) (b)

Figure 4. TEM micrograph for latex：(a) P ($EP-A_6$) J_0；(b) P ($EP-A_6$) $J_{(1:1)}$

4 Conclusion

The epoxy-acrylate latex contains ketone carbonyl is prepared to make the room temperature crosslingking latex by adding ADH into epoxy-acrylate latex. Crosslingking reaction between ketone carbonyl and hydrazine has been proved by FTIR spectra and TEM micrograph of the film. Both explorations for reaction condition of DAAM and ADH and FTIR for simulation of latex forming film indicate that the best pH condition for reaction between ketone carbonyl and hydrazine is alkaline and weak acid.

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