Preparation of hexamethylol melamine resin with low crystallization water and low viscosity for hexamethylol melamine/polyvinyl alcohol composite membrane

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Hexamethylol melamine resins (HMM) with low crystallization water content and low viscosity were prepared by inhibiting the condensation polymerization of low hexamethylol melamine. The effects of catalyst, pH, formaldehyde/melamine ratio, reaction temperature and time on the synthesis parameters of HMM were investigated. The results showed that the sample (HMM8) synthesized with Na_2CO_3-$NaHCO_3$ as catalyst had the crystallization water content lower than 10%, being with a viscosity of about 0.26 Pa·s. The melting temperature of HMM8/polyvinyl alcohol (PVA) curing system was about 164.3 °C. It was found that the higher the amount of formaldehyde, the greater the hydroxyl methyl bounded to each triazine ring. Compared with the traditional melamine formaldehyde resin which had the crystallization water content of about 20–30%, the production of this resin was expected to reduce the energy consumption of industrial reaction, while the resin with 10% crystallization water content was more conducive to the development of alloying HMM/PVA composite membrane.

Keywords: low crystallization water content, low energy consumption, low viscosity, hexamethylol melamine/polyvinyl alcohol, composite membrane.

INTRODUCTION

Hexamethylol melamine resins (HMM) is a kind of white crystalline particle or powder, which belongs to the category of thermosetting resin primary polymer. Under the high-temperature treatment, it changes from soluble to insoluble. HMM is a multifunctional polymer, which is widely used as the treatment agent in the manufacture of coatings, plastics, adhesives and fabric, paper and leather fabrication processes[1–4]. However, there are some issues in the process of its industrial production, including high energy consumption, high pollution and high production cost. On the one hand, when HMM is applied to aminoplasts and urea formaldehyde plastics, if the conversion rate of formaldehyde is not high, it will lead to the release of carcinogens. On the other hand, at present, the crystal water content of the resin product on the market is mostly 20–30% and the viscosity is relatively unstable, which limits the application of the resin. Now people pay more and more attention to health[5] and governments propose stricter supervision on environmental protection[6–7].

The fabrication methods of methyl ether amino resin include the one-step method and two-step method. The one-step method is to complete the hydroxym-ethylation reaction and etherification in the production of amino resin[8]. The resin does not distinguish between alkaline and acidic stages in the reaction process, which indicates that the reaction was always carried out under weak acidic conditions. Its advantages are easy to control, short production cycle and simple operation. However, the resin produced by this method has high crystallization water content and is not easy to store, which leads to high energy consumption[9–10]. Therefore, researchers mostly adopt two-step method. In the two-step process, melamine reacts with formaldehyde to form a mixture with different hydroxyl methyl groups, which is called hydroxymethylation reaction[11]. The next etherification stage is the reaction of hydroxymethyl compounds with alcohols to improve the molecular polarity and form new alkoxy groups. Due to the different groups connected to the triazine ring, the overall properties of melamine resin are also different. Therefore, the two-step hydroxymethyl reaction has attracted the interest of researchers. Sun et al. discussed the conditions for the synthesis of high etherified melamine formaldehyde resins. It was considered that the resin with low crystallization water content was most easily prepared when the molar ratio of melamine and formaldehyde in hydroxymethylation reaction was 1:8[12]. However, no catalyst was used in the reaction. Yin et al. researched the hydroxymethylation steps by adding melamine and excess paraformaldehyde into the reactor. They found that the molar ratio of paraformaldehyde to melamine should be greater than 8. Under normal pressure, the temperature should be controlled at 30–35 °C and the water content should be controlled at 5–15%. The hydroxymethylation reaction was carried out by adding an appropriate amount of manganese dioxide catalyst. Yang et al.[13] researched hydroxymethylation by putting paraformaldehyde, melamine and methanol into the reactor. The final product of hexahydroxymethyl melamine crystallized too fast by adjusting the pH value of 7.5–9.5 with sodium hydroxide and controlling the reaction temperature at 60–70 °C[14]. Masaya Okano et al.[15] believed that under neutral or weakly alkaline conditions, even if the molar ratio of formaldehyde to melamine was greater than 8, hexamethylol melamine may not be generated. On this premise, they proposed the reaction mechanism of melamine and formaldehyde under alkaline, acidic and neutral conditions. It was considered that the reaction mechanism under alkaline conditions was that the nitrogen anion on melamine

attacked the carbonyl carbon on formaldehyde molecule, which was the rate determining step of the addition reaction[16]. Thus, there were many factors affecting the crystal water content of hydroxymethylation reaction products, including raw material ratio, reaction temperature, pH, reaction time, stirring speed and so on. However, in the process of hydroxymethylation, pH of the system decreased, which affected the hydroxymethylation process[17]. At the same time, the molar ratio was so low that the crystalline water content of the synthesized hexamethylol melamine was mostly 20–30%.

HMM resins can be mass-produced at low costs. Resins with low crystalline water content and low viscosity may have new applications, which can well coat red phosphorus particles. Compared with uncoated red phosphorus, the stability of coated red phosphorus was significantly improved. After coating, the water absorption of red phosphorus is reduced, the oxidation resistance is significantly enhanced, and the high-temperature thermal stability is improved. It is suitable for flame retardant of a variety of resins and rubber. It can also be used to synthesize melamine formaldehyde resin (MF) foam, which is often used to prepare aircraft seat, oil and water separator's filter core, sound insulation foam decoration. The product is hydroxylated twice with dihydroxymethylpropionic acid to obtain a hyperbranched polymer with 24 hydroxyl end groups. Then a new hybrid alkyd resin is obtained by reacting with low molecular weight alkyd resin in different proportions. This resin has low viscosity and is easy to flow like oil. At the same time, it is also a solvent-free and anhydrous liquid[18]. This advantage makes the new hybrid alkyd resin more likely to be a high solid, emulsion type, water dispersoid and non-aqueous dispersion alkyd paint.

In this work, melamine and formaldehyde were used as raw materials, sodium carbonate-sodium bicarbonate was used as a catalyst to inhibit the change of pH, to prevent the polycondensation between hydroxymethyl reactions. Without using paraformaldehyde and sodium hydroxide as the catalyst, HMM with low crystallization water content (9.2%) and low viscosity (0.26 Pa·s) were successfully prepared. The crystallinity and melting temperature of HMM/polyvinyl alcohol (PVA) were also studied.

EXPERIMENTAL

Materials

The following chemicals were purchased from various companies and were used without further purification. Polyvinyl alcohol(PVA), melamine(CP), sodium hydroxide, sodium carbonate and sodium bicarbonate were all from traditional Chinese Medicine Chemical Reagent Co., Ltd., while formaldehyde (37%) was from Sinopharm chemical group Reagent Co., Ltd.

Preparation of hexamethylol melamine

Preparation of prepolymers: HMM was synthesized according to the molar ratio of melamine: formaldehyde: water of 1:10:50. 6.3 g melamine, 38 ml formaldehyde solution (37%) and 21 ml water were added sequentially into the round-bottom flask at room temperature. The mixture was stirred at 300–400 rmp, heated to 80 °C, maintained at 80 °C after 10–30 min of stirring.

Separation of HMM: the above mixture was continuously stirred and the pH of the reaction system was kept at 8.3–8.4 with buffer solution. The sodium carbonate-sodium bicarbonate buffer solution was prepared by mixing 0.1 mol/L sodium carbonate aqueous solution and 0.1 mol/L sodium bicarbonate aqueous solution in the volume ratio of 4:6. When melamine in the reaction system was completely dissolved, the reaction stirring speed was reduced to 200–300 rpm and the reaction was maintained for 3 h. After stopping stirring and standing for crystallization for 1.2 h, the waste liquid was filtered and separated, then dried to obtain the finished white granular solid hexamethylol melamine. The final product of hexamethylol melamine was sampled and dried in the oven at 60 °C for 2 h. Considering that the total crystallization rate is determined by nucleation and growth rate, to obtain better crystal form, the seed and hexamethylol melamine were added before crystallization. HMM samples prepared under different conditions are named HMMx, where x is the serial number of the samples listed in Table 1.

Preparation of hexamethylol melamine/polyvinyl alcohol membrane

Water with mass ratio w(water):w(polyvinyl alcohol) of 5:1 and polyvinyl alcohol were added into the beaker. After magnetic stirring for 30 min, the whole system was put into a 90 °C water bath and stirred for about 10 min. When there was no gel polyvinyl alcohol in water solution, the mixture was heated and stirred in the water bath at 90 °C in continuous, and an appropriate amount of the above hexamethylol melamine was added. After the solution was clarified, the sample was taken quickly with a straw and the solution was dropped on an inclined glass slide to make the solution automatically coated on the glass slide. Then, the membrane was cured in a constant temperature oven.

Research methodology

In a typical experiment, about 17.00 g HMM8 was put into a 50 ml centrifuge tube and the same mass of waste liquid was taken into another centrifuge tube for centrifugation balance. The high-speed centrifuge H1850 was used for centrifugation 3–5 times. The speed of separation was 8000 rpm and the durations were 5 minutes. After centrifugation, the mother liquor was removed and its mass was 16.09 g (M_c). Then it was dried and crystallized in the oven at 60 °C for 2 h, and its mass was 14.53 g (M_d). The crystal water content is calculated by the equation $M_x = (M_c - M_d)/M_c$, where M_x is the crystal water content, M_c is the mass of HMM

Table 1. Conditions Used for The Synthesis and Crystallization of HMM Materials in This Work

Samples	Mixture ratio	Reaction temperature (°C)	pH	Catalyzer	Drying time (min)	Drying temperature (°C)	Crystal water content (%)
HMM1	1:7:30	60	7.9	NaOH	60	40	24.5
HMM2	1:7:35	60	7.9	Na_2CO_3-$NaHCO_3$	60	40	23.6
HMM3	1:8:30	60	8.2	NaOH	75	50	16.4
HMM4	1:8:35	70	8.2	Na_2CO_3-$NaHCO_3$	100	50	14
HMM5	1:9:40	70	8.3	NaOH	100	50	13.8
HMM6	1:9:45	75	8.3	Na_2CO_3-$NaHCO_3$	120	60	12.5
HMM7	1:10:45	75	8.3	NaOH	120	60	10.2
HMM8	1:10:50	80	8.3	Na_2CO_3-$NaHCO_3$	120	60	9.2
HMM9	1:12:50	80	8.5	NaOH	150	60	13.3
HMM10	1:12:60	80	8.5	Na_2CO_3-$NaHCO_3$	150	60	12.6

after centrifugation and M_d is the mass after dry crystallization.

Similarly, about 25 mg HMM8 was put into a constant temperature bath and kept for a period of time to balance the resin temperature with the test temperature. The lifting knob was rotated to lower the instrument slowly. Then, the rotor was gradually immersed into the liquid to measure until the liquid level mark of the rotor was flushed with the liquid level. The motor and the knob were turned on before the pointer was stable and each sample was measured three times. The average value of the three samples was about 0.052 Pa·s, and the specific coefficient of rotor speed k was 5. Viscosity of HMM8 was calculated by the equation $\eta = k \cdot \alpha$, where η is viscosity, k is the coefficient, α is the reading indicated by the pointer.

The ^1H NMR of raw materials and products was tested by ^1H NMR spectrometer under the condition of frequency of 400MHz and solvent of DMSO. Fourier transform infrared spectroscopy (FTIR) was a characterization technology that can determine the chemical bonds and functional groups in unknown compounds and then determine their chemical structure. After the sample was mixed with diluent KBr and pressed into tablets, it was tested and analyzed on the Nicolet 6700 infrared spectrometer produced by Themro Fisher company. The wavelength range was 4000 cm^{-1} – 400 cm^{-1} and the resolution was 4 cm^{-1}. The scanning electron microscope (SEM) image of SU8010 made by Hitachi was used. Before the measurement, the sample was sprayed with a layer of gold powder. The crystallinity of the system was determined by differential scanning calorimetry. The HMM of 0.2 mg was put into the aluminum crucible and put into the Differential Scanning Calorimetry(DSC) sample pool. The melting point was measured at the heating rates of 30 ºC/min, 20 ºC/min and 10 ºC/min, the starting crystallization temperature and crystallization peak temperature were measured at the cooling rates of 2.5 ºC/min, 5 ºC/min, 10 ºC/min, 15 ºC/ min and 20 ºC/min. The test was carried out in N_2 atmosphere with a flow rate of 40 ml/min.

RESULTS AND DISCUSSION

Structural characteristics

Different conditions used for the synthesis of HMM such as reaction temperature, melamine / formaldehyde / water molar ratio, pH and the type of catalyst were summarized in Table 1. Table 2 gives the effect of formaldehyde dosage on hydroxymethyl reaction.

It is seen from Table 2 that formaldehyde and melamine react according to different molecular ratios to produce hydroxymethyl melamine with different hydroxymethyl groups. If formaldehyde is excessive to a certain extent, six hydroxymethyl groups can be formed theoretically. It could also be found that the higher the amount of formaldehyde, the greater the hydroxyl methyl base of each triazine ring. To obtain hexamethylol melamine, the equimolecular ratio of formaldehyde to melamine must be more than 1:8. Taking into account the possible uncertainties in production, it could be enlarged to more than 1:10.

Table 2. Effect of Formaldehyde Dosage on Hydroxymethyl Reaction

Melamine/Formaldehyde (equimolecular ratio)	Number of hydroxymethyl groups bound to triazine ring
1:1	1.2
1:2	1.8
1:3	2.8
1:4	3.6
1:5	4.5
1:6	5.2
1:7	5.8
1:8	5.9

Figure 1 shows the variation relationship of crystallization water content of HMM samples in Table 1 under different conditions. It can be seen intuitively that molar ratio, pH, reaction temperature and drying time had a great impact on the crystal water content of the finished product[19]. The curves of molar ratio, pH and drying time all had extreme points, indicating that the horizontal value range of these factors just includes the optimal value. Therefore, too high and too low values of these factors could affect the crystal water content of the final product. The effect of the molar ratio was that the content of crystal water increased when the ratio was lower than 1:10[20]. It was reasonable to predict

that if the ratio continued to decrease, the crystal water content may further increase. In view of the binding relationship between triazine ring and hydroxymethyl group in Table 2, to obtain hexamethylol melamine with low crystalline water content, the molar ratio was improved to 1:10 based on 1:8. While, the value of the final optimization condition needed to be determined by the analysis of pH, reaction temperature and drying time.

The synthesis conditions affected the structural properties of synthesized polymers. Scheme 1 represents the crosslink processes for the synthesis HMM resins. Four stages can be expected: (1) the main reaction of hydroxymethylation, (2) dehydration condensation reaction, (3) canizzro reaction and (4) synthesis of trimethylolmelamine and hexahydroxymethylmelamine. Specifically, the —CH_2OH formed by reaction in acidic medium was prone to dehydration condensation reaction with unreacted amino (—NH_2) and imino (—NH—) in melamine. When the condensation degree was large enough, gels could occur. Thus, hydroxymethylation must be carried out in alkaline environment. Based on the fact that the hydroxymethyl reaction was carried out under alkaline conditions when the pH was less than 8, the reaction was slow and it was easy to polycondensate between hydroxymethyl groups[21]. When pH was greater than 8.5, the reaction was so fast that the polyhydroxymethyl product crystallized quickly and the reaction was incomplete. Thus, pH was the important factor affecting the crystal water content of synthesized HMM materials. It could be seen from Figure 1c that when pH increased from 7.9 to 8.3, the content of crystalline water continued to decrease. When pH was gradually higher than 8.3, the content of crystalline water tended to increase. This was due to canizzro reaction of formaldehyde at high pH[22]. Free formaldehyde combined with alkali to form salt and methanol, which did not react with melamine, so the content of crystal water decreased, indicating that at pH 8.3, the reaction rate was appropriate, there were few side reactions and the content of crystal water was low. Generally speaking, the reduction of formaldehyde means the formation of hydroxymethyl groups. There is more free formaldehyde in the product and the content of crystal water is low. However, by comparing the four diagrams in Figure 1, it could be found that there was no extreme point in the relationship between reaction temperature and crystal water content. In consideration of this factor, it could be found that the increase of temperature and the slow addition rate of melamine led to the low content of crystal water in the final product, indicating that there was more formaldehyde reaction. But the degree of hydroxymethylation of the product was not high, indicating that all the reacted formaldehyde did not exist in the form of hydroxymethyl and some of them became by-products. With the increase of temperature, the reaction speed was obviously accelerated and the content of crystal water was gradually reduced (Figure 1b). As the reaction product changed from hydrophilic to hydrophobic with the progress of the reaction, the change trend of crystal water content was not obvious at a certain time. When the reaction was carried out at a low temperature of 60 °C, the dissolution of melamine took a long time, indicating that the

hydroxymethylation reaction was slow. When the reaction was carried out at a higher temperature of 80 °C, melamine was completely dissolved in only 10 minutes and the crystal water content of the final product was less than 10%. The above comparison showed that the reaction rate varied greatly with different temperatures. Therefore, when the reaction was carried out at higher temperature, it was more conducive to the formation of hexamethylol melamine with low crystal water content, indicating that it was suitable to control the hydroxymethylation temperature at 75–80 °C. The influence of drying time on crystal water content was also very important[23]. It could be seen from Figure 1d that the crystal water content decreased rapidly within 60–80 minutes, the decreasing trend of crystal water content became stable within 90–120 minutes and the crystal water content increased after 120 minutes. Because of that, there were two coexisting processes of crystal nucleus growth and crystal growth in the crystallization process, the extension of crystallization time was conducive to crystal growth. Consequently, the rapid growth of crystal within 60–80 minutes made the crystal water content decrease rapidly. When the drying time was 90–120 minutes, the solution may continue to maintain the crystal growth state without spontaneous nucleation. However, when the drying time was more than 120 minutes, the crystallization time was long, which caused too much crystal nucleus growth and in turn make the crystal unable to continue to grow, so the crystal water content tended to increase. Therefore, controlling the appropriate drying time was more conducive to the formation of HMM with low crystal water content.

The optimum reaction conditions were as follows: the ratio of raw materials was 1:10:50, the reaction temperature was 75 °C, the pH was 8.3 and the drying time was 120 min. Under the optimal conditions, the degree of hydroxymethylation of the product can reach 5.9 and the content of crystal water is 9.2%.

According to the analysis of the morphology of the HMM produced by the reaction at different molar ratios, the SEM images at the same magnification (30000 times) are shown in Figure 2[24]. It can be seen from Figures 2c and d that all the HMM with different proportions have a crystal structure. Specifically, with the increase of formaldehyde content, the particle size of HMM became smaller and arranged more orderly, indicating that the reaction rate between formaldehyde solution and melamine decreased significantly. The formation rate of HMM becomes slower, which is conducive to the formation of more small crystal nucleus in the case of slow reaction. Therefore, the number of crystal nucleus is the key to obtaining crystalline products with small and uniform particle sizes. In addition, the HMM crystals formed by the continuous reaction are gradually enriched on the crystal nucleus, which makes the microstructure of dried HMM powder more neat and fine. However, the system with high molar ratio has less formaldehyde content and faster overall reaction speed, which makes the rate of crystal nucleus formation in the system too large and there is no time to produce more crystal nucleus in the solution[25]. Thus, a large number of HMM crystals are enriched and gathered together,

(1) The main reaction of hydroxymethylation:

(2) Dehydration condensation reaction:

(3) Canizzro reaction:

$$2CH_2O + OH^- \longrightarrow HCOO^- + CH_3OH$$
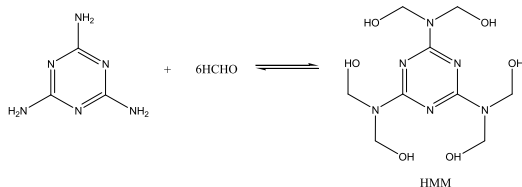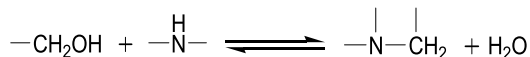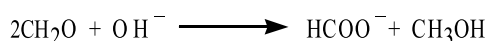
(4) Trimethylolmelamine and hexahydroxymethylmelamine:
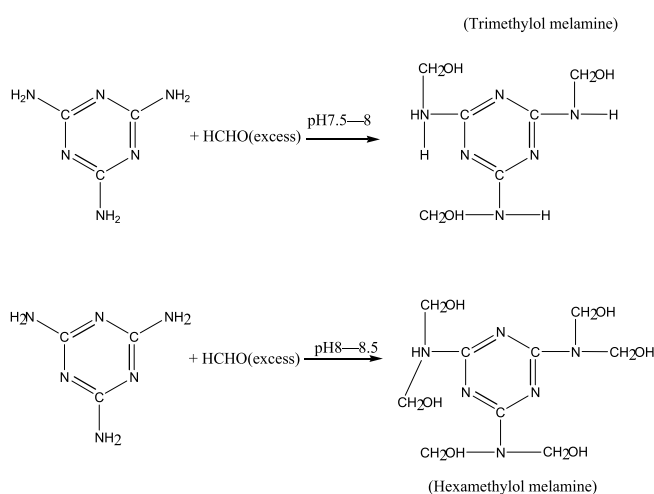
Scheme 1. Possible reactions for the synthesis of HMM

which makes the microstructure of dried HMM powder more disordered and larger.

Another possible reason why SEM test results show this law is that the —CH_2OH groups formed by the first addition passivate the activity of adjacent amino H during the reaction of formaldehyde with —NH_2 in melamine[26, 27]. Due to the high formaldehyde content at low molar ratio, the activity time of —CH_2OH groups passivating adjacent amino H is longer, which results in the slow formation of hexamethylol melamine, enough time to generate more small crystal nucleus. Then, the subsequent polyhydroxymethylated melamine is slowly enriched on the crystal nucleus. Thus, the particle size of HMM prepared at low molar ratio is small and arranged neatly. Moreover, each HMM molecule contains six —CH_2OH, the hydroxyl groups of six —CH_2OH are not only associated with adjacent groups but also are associated with hydroxyl groups in other molecules in the system through hydrogen bond[28]. The water in the system also has —OH structure and the water molecule contains two —OH, so the six —CH_2OH of HMM are easier to agglomerate together through hydrogen bond in water to form a floc system[29]. This strong agglomeration makes the size of particles smaller and more regular. At the same time, the strong agglomeration also causes the overlapping of flocs and flocs to form a network structure.

Figure 3 shows the infrared spectrums for the melamine and hexamethylol melamine. The most direct change of HMM8 formed by the addition of melamine and formaldehyde was the disappearance of N-H and the formation of -CH_2OH[30]. The strong absorption peak at 3336 cm^{-1} corresponded to the tensile vibration of -OH. The peak at 2968 cm^{-1} was caused by the hydrocarbon stretching vibration of hydroxymethyl group, 1566–1390 cm^{-1} was
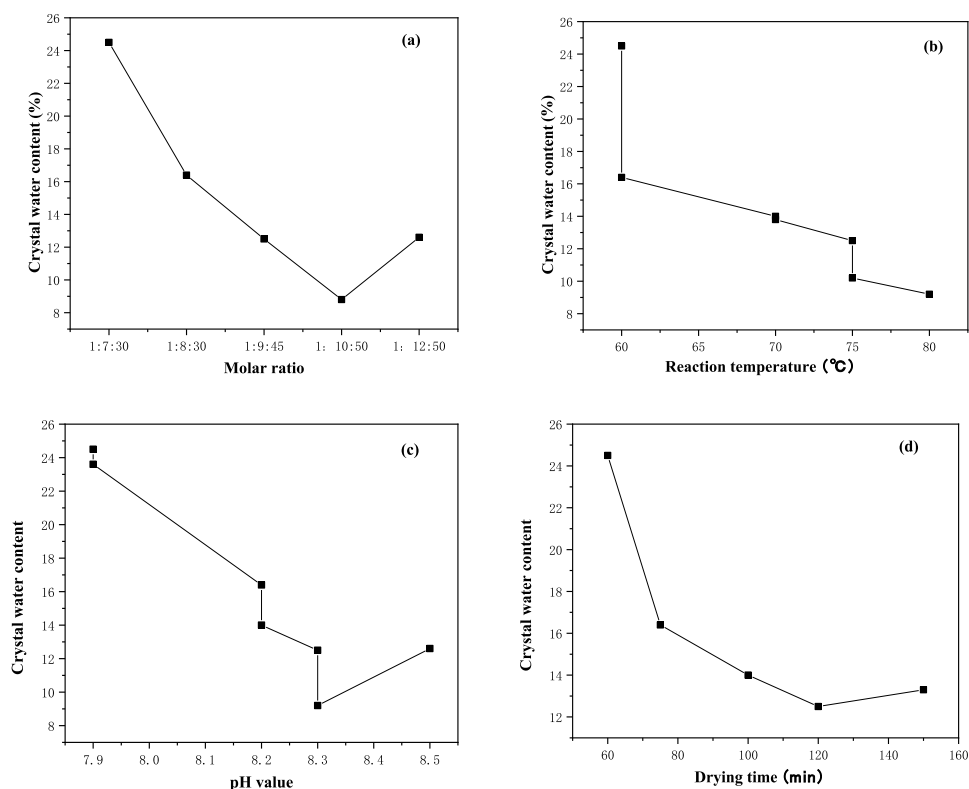
Figure 1. The crystallized water content of the synthesized HMM under different molar ratio (a), reaction temperature (b), pH value (c) and drying time (d)
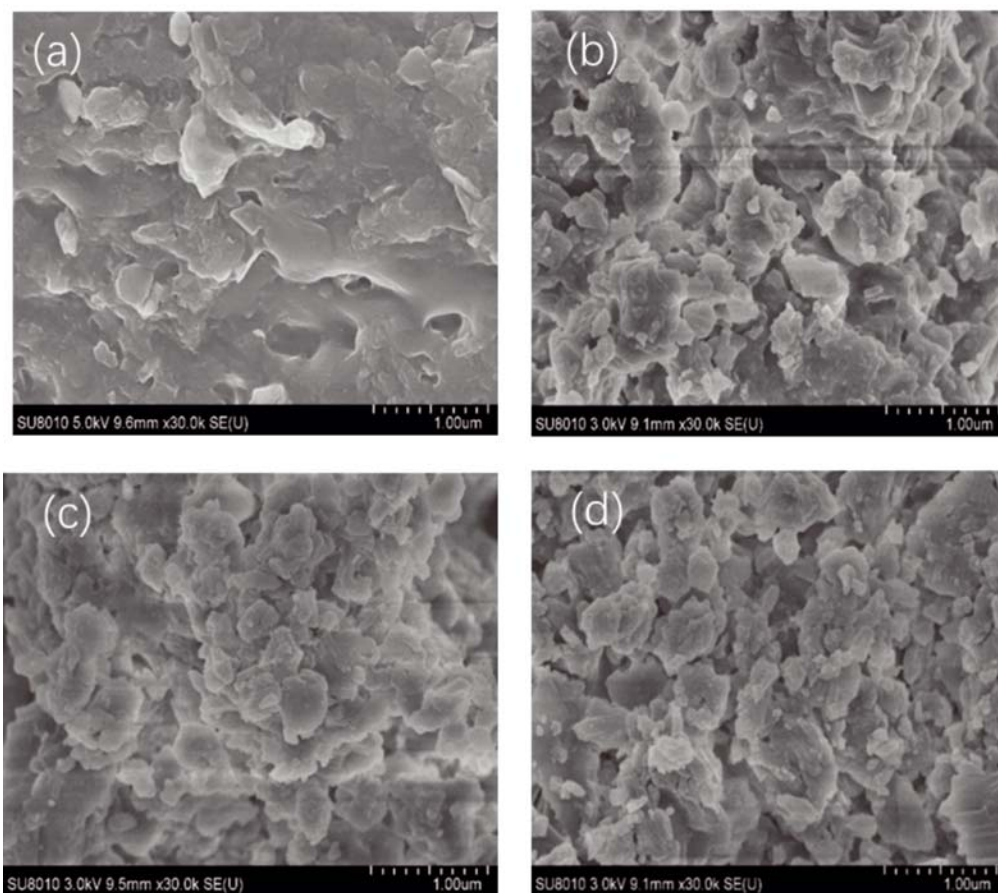
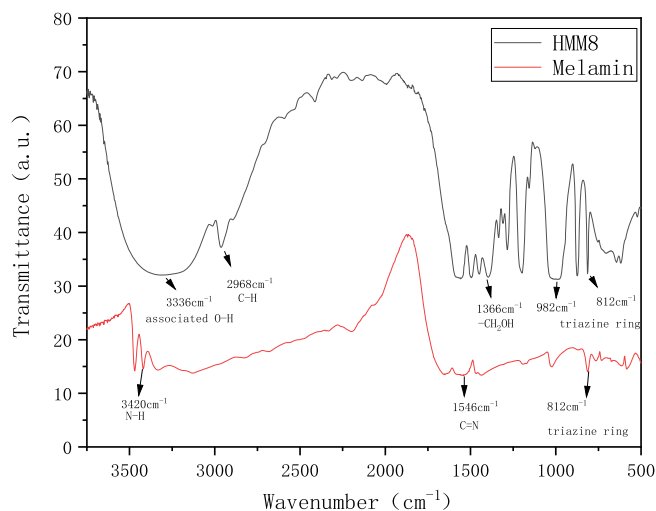**Figure 2.** High resolution SEM images for the HMM1 (a), HMM3 (b), HMM6 (c) and HMM8 (d)

Figure 3. FTIR spectrums of the HMM8 and melamine

the characteristic absorption peak of C=N stretching vibration, 982 cm⁻¹ was the characteristic absorption peak of C-O bending vibration and the peaks at 540 cm⁻¹ and 812 cm⁻¹ were attributed to the C-H stretching vibration and the bending vibration of triazine ring[31], respectively. The above analysis showed that HMM was formed in the reaction.

Through ^{1}H NMR spectrometer, melamine(a) and HMM8(b) were tested under the condition of 400 MHz frequency and DMSO solvent. The results were shown in Figure 4. The chemical shift of melamine(a) was: δ = 3.83 (s, 6H, N-H), the chemical shifts of HMM8 were: δ = 6.15 (d, H, -OH), δ = 3.38 (s, 2H, -CH₂OH), δ = 2.51 (s, H, C-H). The results of ^{1}H NMR analysis
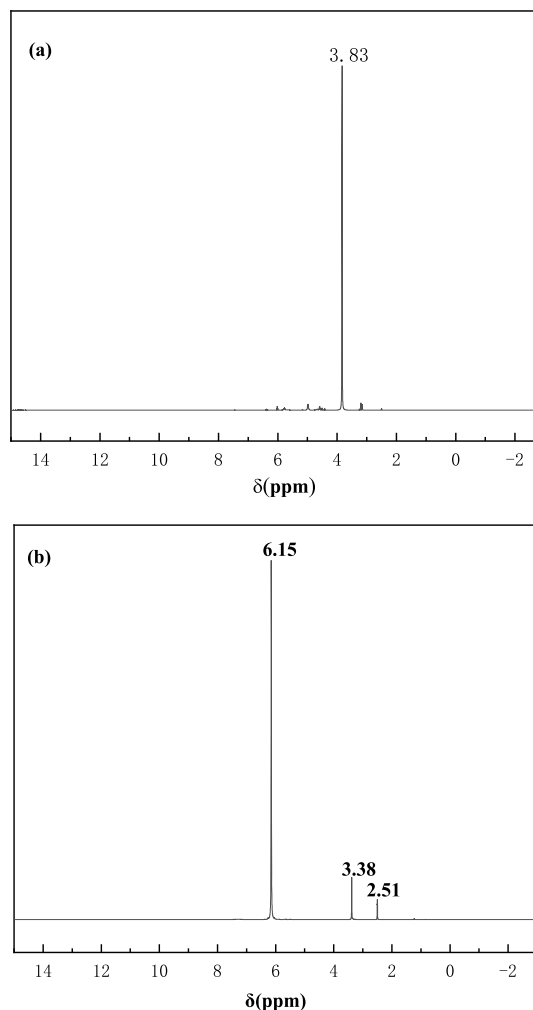

Figure 4. ^{1}H NMR spectra of melamin (a) and HMM8 (b)

of melamine and HMM8 were compared, the ^{1}H NMR spectrogram of melamine only detected hydrogen in one chemical environment, which was H on the N-H functional group unique to melamine. With the synthesis of HMM8, the hydrogen of its specific functional group -CH2OH was detected in ^{1}H NMR, and the chemical shift shifted to the high field. The results showed that HMM8 had been successfully synthesized. Because there were basically no impurity peaks in the NMR spectrum, it showed that the synthesized product had high purity. This was consistent with the infrared results.

Crosslinking degree of polyvinyl alcohol (PVA) / HMM solution cured membrane

The crosslinking degree of resin is an important index in the application. Therefore, experiments were designed to test the film formation of PVA/HMM8 system under different ratios, different curing temperatures and the same heating time. The crosslinking degree of the film was measured by the swelling method. The test results were shown in Table 3. The relationship between crosslinking degree α and curing temperature was shown in Figure 5.

Table 3. Crosslinking Degree of Films Formed with Different Weight Ratio and Temperature

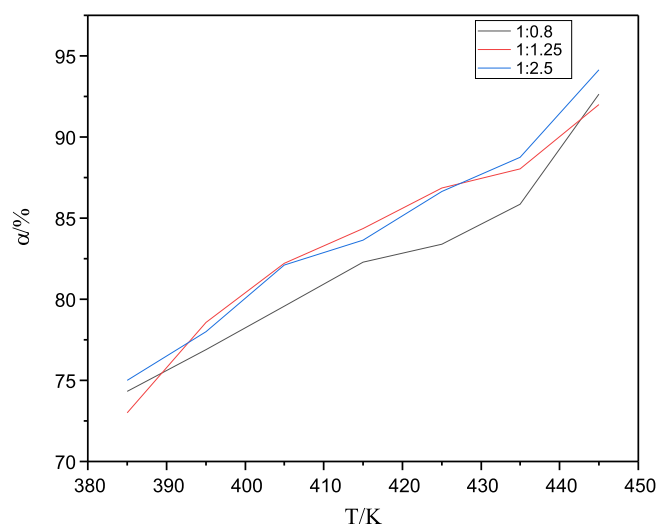| Temperature (T/K)	Different weight ratio α/%		
	1:0.8	1:1.25	1:2.5
385	74.30	73.00	75.00
395	76.89	78.56	78.00
405	79.59	82.23	82.10
415	82.28	84.36	83.66
425	83.39	86.88	86.65
435	85.86	88.03	88.78
445	92.65	92.03	94.16

Figure 5. The relationship between crosslinking degree α and curing temperature

It was shown that the plot lines with complex ratios of 1:0.8, 1:1.25 and 1:2.5 had similar intercept and slope, which can be approximately regressed to α = 0.287 T – 36.4. The law of compound curing can be explained by phenomenological model: the correlation between crosslinking degree and the proportion of compound system was small, but mainly related to curing temperature. HMM, commonly known as melamine, was a widely used chemical intermediate product with the

advantages of non-toxic, good insulation and so on[32]. It was a triazine nitrogen-containing heterocyclic compound. The triazine ring in the molecule had strong rigidity. It reacted with formaldehyde to form melamine resin, which was further crosslinked into a three-dimensional network structure, so it had high wear resistance and hardness. PVA was easy to be prepared into water-soluble adhesive, which was one of the bulk products for the synthesis of water-soluble adhesive. Compared with traditional adhesives, its products had the advantages of more stable quality, cheaper price and more environmental protection, and had a good competitive advantage. HMM was made from formaldehyde and melamine, and then compounded with polyvinyl alcohol as base agent to impregnate fiber, which can be used to make new composite reinforcement. In addition, melamine adhesive had the advantages of low curing temperature, strong wear resistance and excellent weather resistance in bonding wood[33]. It was of great significance in wood recycling and comprehensive utilization.

Crystallization characteristics

The melting curves of PVA/HMM8 at different heating rates are shown in Figure 6. When the heating rates were at 10 ºC/min and 20 ºC/min, there were obvious double peaks. At 10 ºC/min, there was obvious rebound after the first peak, while at 20 ºC/min, the first peak was almost flat without rebound. This was because the melamine impurity possibly contained in HMM8 affected the molecular binding energy on the crystal surface so that some crystals could not grow and were not affected by temperature[34]. When the heating rate gradually increased to 30 ºC/min, there was only one melting peak at 164.3 ºC. The reason was that the PVA/HMM8 was composed of the perfect crystallization part and imperfect crystallization part. When the heating rate was small, the resin with imperfect crystallization began to melt and a melting peak appeared. With the increase of temperature, the melting of the imperfect crystallization part was almost completed and the PVA/HMM8 with perfect crystallization gradually began to melt, then a melting peak appeared again. However, when the heating rate was large enough, the temperature rose rapidly when the PVA/HMM8 with imperfect crystallization began to melt, and there was a delay effect between melting and temperature. This made the melting process of the perfect crystallization part and the imperfect crystallization part almost simultaneously, so there was only one melting peak in the melting process. Thus, the heating rate was extremely important. On the other hand, impurity ions could adhere to the surface of the newly formed crystal nucleus and hinder the growth of the crystal nucleus, so that the crystal could not grow. Therefore, the qualitative transformation from double peak to single peak was realized. This also provided great help for the change of phase transition characteristics by adjusting impurities or improving the purity of materials.

The DSC crystallization curves of unsaturated PVA/HMM8 under different cooling rates are shown in Figure 7. Through the analysis of DSC results[35], the starting crystallization temperature T_0, crystallization peak temperature T_p, ending crystallization temperature
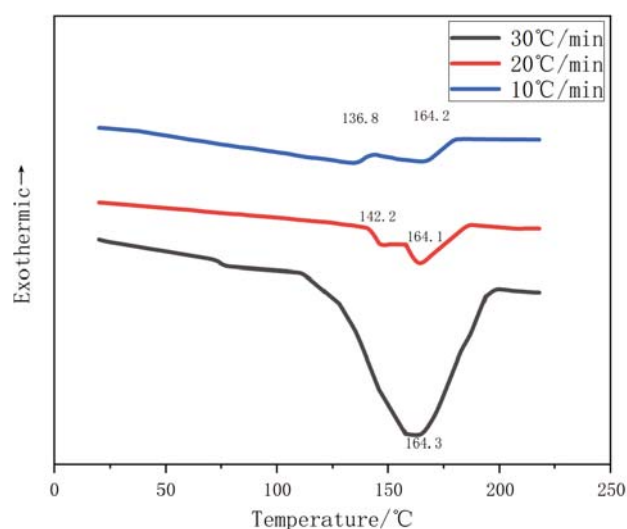
Figure 6. Melting point test results at different heating rates

Figure 7. DSC crystallization curves at different cooling rates

T_1 and corresponding glass transition temperature T_g of PVA/HMM8 are shown in Table 4 ($\Delta T = T_1 - T_0$). It can be seen from Table 4 that with the acceleration of cooling rate, the PVA/HMM8 crystallization temperature T_0 and crystallization temperature T_1 both showed a decreasing trend. This showed that increasing the cooling rate helped to reduce the initial crystallization temperature of the PVA/HMM8, which was of great help to reduce industrial energy consumption. From the trend of glass transition temperature T_g, we could find that the decrease of T_g was not obvious with the increase of cooling rate. Specifically, glass transition was an important characteristic of polymers, the glass transition temperatures at 2.5 °C·min^{-1} and 5 °C·min^{-1} were greater than 10 °C. At this time, the amorphous part of the PVA/HMM8 began to change from frozen state to thawed state, which was a relaxation phenomenon[36–39]. From 10 °C·min^{-1} to 20 °C·min^{-1}, the glass transition temperature was below 10 °C. At this time, the PVA/HMM8 was in the glass state, the molecular chain and chain segment could not move, but the atoms or groups constituting the molecules vibrate at their equilibrium position. After the glass transition temperature continued to decrease, although the molecular chain could not move, the chain segments began to move and show high elastic properties. If the cooling rate increased again, the whole molecular chain may move and show viscous flow properties[40, 41]. Glass transition temperature (T_g) fully expressed an important physical property of amorphous polymers and it was also a key factor controlling material deformation.

Table 4. The Initial Crystallization Temperature T_0, Crystallization Peak Temperature T_P, End Crystallization Temperature T_1 and Glass Transition Temperature T_g of PVA/HMM8

Cooling rate/(°C·min^{-1})	T_0/°C	T_p/°C	T_1/°C	T/°C	T_g/°CΔ
2.5	58.4	63.8	68.8	10.5	15.8
5	45.5	52.8	58.9	13.4	10.6
10	41.0	52.4	62.1	21.1	7.3
15	32.2	45.4	55.6	23.4	5.6
20	25.0	40.6	52.8	27.8	2.5
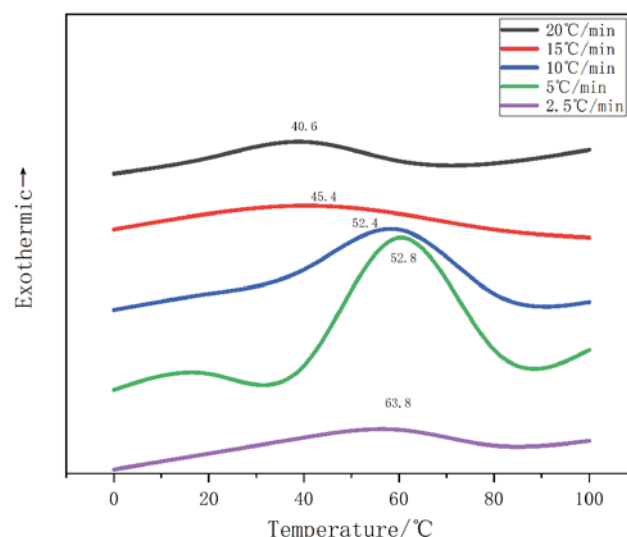
According to the parameters in Figure 7 and Table 4, it can be seen that when the cooling rate increased from 2.5 °C/min to 20 °C/min, the crystallization peak temperature decreased from 63.8 °C to 40.6 °C, which was nearly 40%. The width of the crystallization peak increased from 10.5 °C to 27.8 °C, which was about two times. Obviously, with the increase of cooling rate, the crystallization peak temperature gradually decreased and the crystallization peak also gradually widened. At the same time, the glass transition temperature of unsaturated PVA/HMM8 decreased with the increase of cooling rate[42, 43]. Because when the cooling rate was small, the molecular chain of unsaturated PVA/HMM8 had a longer time at high temperature and the kinetic energy of the molecular chain was greater. With enough time to arrange, the molecular chain could be more regular and the crystallization could be more perfect. So the crystallization peak of PVA/HMM8 appeared at higher temperature and the peak type was narrow and sharp. Specifically, there was a delay between the crystallization process and the temperature decrease, the greater the cooling rate, the greater the delay between the resin crystallization and the temperature decrease. Therefore, when the cooling rate was large, the molecules stayed in the high-temperature section for a short time and the molecules could not be arranged regularly. It was possible that crystallization was still proceeding when the temperature was lowered to a lower temperature. Hence, the starting temperature of crystallization was lower and the crystallization peak was broad and flat. In recent research, Zhan et al[44]. used the differential scanning calorimetry (DSC) to measure the nonisothermal crystallization behavior of carbon fiber reinforced polyether ether ketone (CF/PEEK) composites under different cooling rates. The characteristic parameters of crystallization were obtained, and the nonisothermal crystallization model was established. The crystallization temperature range of the material at different cooling rates was predicted by the model. The unidirectional laminates were fabricated at different cooling rates in the crystallization temperature range. The results showed that the crystallization temperature range shifted to a lower temperature with the increase of cooling rate, the establi-

shed nonisothermal crystallization model was consistent with the DSC test results. It was feasible to shorten the cooling control range from the whole process to the crystallization range. The crystallinity and transverse tensile strength declined significantly with the increase of the cooling rate in the crystallization temperature range. The research results provided theoretical support for the selection of cooling conditions and temperature control range, which could be applied to the thermoforming process of semi-crystalline polymermatrixed composites to improve manufacturing efficiency.

CONCLUSIONS

HMM with low crystalline water content (9.2%) and low viscosity (0.26 Pa·s) were prepared under the condition of inhibiting the change of reaction pH. formaldehyde/melamine ratio, catalyst, pH and reaction temperature were the main factors affecting the structure of synthetic HMM materials. When Na_2CO_3-$NaHCO_3$ was used as catalyst, the molar ratio of melamine, formaldehyde and water was 1:10:50, the HMM materials had the lowest crystalline water content and the lowest viscosity.

Infrared spectroscopic and SEM results showed that there are abundant -CH_2OH and triazine rings on the surface of HMM. The active H in -CH_2OH causes polycondensation, which is also the key factor affecting the stability of the resin. After the hydroxymethylation of melamine and formaldehyde, if the reaction product can be etherified with alcohol in time, alkyl can be used to replace the active hydrogen atom in hydroxymethyl. That is, sealing the active hydroxymethyl group can greatly reduce the progress of various polycondensation reactions in structure, to obtain a more stable resin. Etherified melamine formaldehyde resin can better improve the adhesion between coatings on automobile surface and improve the fluidity and leveling of coatings. With the development of China's automobile industry and increasing attention to environmental protection, the development and research of methanol etherified melamine formaldehyde resin has become an important topic in the field of coating resin research. DSC results show that there are two melting peaks when the heating rate is small. With the increase of heating rate, the two melting peaks gradually approach. At the heating rate of 30 °C/min, the unsaturated PVA/HMM8 has only one melting peak and the melting point is 164.3 °C. It can be seen that the heating rate is extremely important, which provides basic data and technical support for the actual operation. The nonisothermal crystallization behavior of carbon fiber reinforced polyether ether ketone (CF/PEEK) composites under different cooling rates showed that cooling rate is an effective method to control the crystallization process. It also paves the way for studying how the rate of cooling crystallization affects the nucleation and growth of crystals in the crystallization process.

Moreover. The PVA/HMM8 with low crystalline water content had a more stable melting point (164.3 °C), indicating that a highly stable HMM resin solution had been synthesized, which might solve the problem of instability of the resin solution for a long time and provide a great convenience for the application of the product in the industrial field.

CONFLICT OF INTEREST

The authors declare no competing financial interest.

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