

SYNTHESIS, CROSSLINKING MECHANISM AND PROPERTIES OF A POLYACRYLATE/POLYURETHANE COMPOSITE COATING

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ABSTRACT

A polyacrylate/polyurethane (P(A)/P(U)) composite coating has been prepared by crosslinking an acetoacetylated polyacrylate with a vinylic group terminated polyurethane at room temperature. A model Michael reaction between ethyl acetoacetate (EAA) and methyl acrylate (MA) was designed to study the crosslinking mechanism. It was found that the two active hydrogen atoms in acetoacetyl group can both add to vinylic groups and the yield of mono- and bis-adducts are much affected by the molar ratio of acetoacetyl to vinylic groups. Higher crosslinking degree and better properties could be obtained with decreasing the molar ratio of the two active groups from 1/1 to 0.6/1 in the composite coatings.

INTRODUCTION

Acetoacetylated resins have attracted much attention in coating, adhesion and sealing industries for the past decade because the presence of acetoacetyl group in the resins could provide improved properties for applications, such as lowering viscosity and increasing adhesion to the metal surface. This group has two reactive sites, active methylene and ketone carbonyl, which are capable of reacting with diamines, melamine, aldehydes, isocyanates, activated olefins and chelation with metals. So the incorporation of the acetoacetyl group onto polymer could provide various routes for modification or crosslinking of polymers^[1-4]. For example, some new thermosetting coatings have been prepared recently by crosslinking of acetoacetylated polyacrylates with activated olefins^[4-6]. However, the crosslinking mechanism in these systems is not fully understood.

In this paper, we synthesized a polyacrylate/polyurethane (P(A)/P(U)) composite coating by crosslinking of an acetoacetylated polyacrylate with a vinylic-ended

polyurethane under room temperature. The crosslinking mechanism between these two polymers was studied by using a model Michael reaction between ethyl acetoacetate (EAA) and methyl acrylate (MA).

EXPERIMENTAL

Preparation of acetoacetylated polyacrylate (P(A))

Acetoacetylated polyacrylate was prepared by copolymerizing of acetoacetoxymethyl methacrylate (AAEM, available from EASTMAN Chem. Co.), styrene (St) and butyl acrylate (BA) in toluene initiated by BPO in a 250 ml flask equipped with a stirrer, a dropping funnel and a reflux condenser. The final solid content in the solution was about 70%. The molecular weight of the copolymer was determined by VPO method.

Preparation of NCO-free vinylic-ended polyurethane (P(U))

P(U) was synthesized by three steps as follows: Firstly, by condensation polymerization, an excess amount of toluene 2, 4-diisocyanate (TDI) reacted with trimethylolpropane (TMP), and polyethylene glycol (PEG) in methyl ethyl ketone (MEK) to form a NCO-ended polyurethane. Then, suitable amount of hydroxypropyl acrylate (HPA) was added and the reaction was carried out continuously for desired time. Finally, excessive methanol was added and reacted with the residual isocyanates. During the reaction, aliquot portions of reaction samples were withdrawn and analyzed for the NCO content by titration method.

Model Michael reaction between EAA and MA

The Michael reaction between EAA and MA was taken place in toluene at $25.0 \pm 0.1^\circ\text{C}$ with 1,8-diazabicyclo (5.4.0)undec-7-ene (DBU, $pK_b = 12.5$) as catalyst and o-dichlorobenzene as internal standard. Reaction aliquots were withdrawn at suitable reaction interval and quantitatively analyzed by GC. The products of mono- and bis-adduct were further confirmed by HP5970 GC-MSD without detecting of any other by-products.

Synthesis of P(A)/P(U) composite coating

Suitable amount of P(A), P(U) and DBU were mixed thoroughly and coated on a steel plate. After dried at room temperature, the crosslinking degree and the properties of the composite coatings were determined.

RESULTS AND DISCUSSION

Synthesis of P(A) and P(U)

For synthesizing P(A) with a homogeneous distribution of molecular structure, a semi-continuous charging method of monomers was employed as follows: firstly, 1/3

part of the mixture of monomers and initiator was added into the system at reaction temperature, then the remaining mixture was added continuously for about 1.5 h. After reacted for further 5 h, the reaction was completed. In order to fit the need for application, the viscosity of P(A), which is mainly governed by the molecular weight of the copolymer, should be controlled at a lower value for a high solid content system. The influences of the amount of BPO on the solid content, molecular weight and viscosity of P(A) were studied and summarized in Table 1.

Table 1 Influence of BPO on the molecular weight and the flowing viscosity of polyacrylate

Amount of BPO (wt%)	0.6	1.0	1.4	1.8
Solid content (%)	70.1	72.3	70.7	71.6
$\bar{M}_n$ of P(A)	10242	7858	4762	4126
Flowing viscosity ^{a)} of P(A) (sec)	difficult to flow	1298	276	289

Conditions: weight ratio, AAEM: St: BA=20:40:40; solvent, toluene; temperature, 118°C; theoretical solid content, 70%; a) determined at 25°C

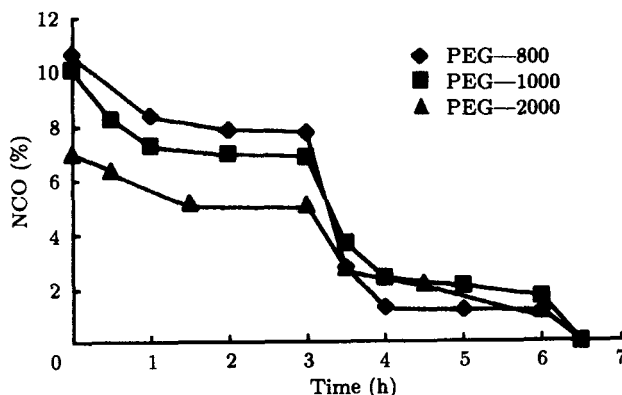


Fig. 1 Relationship between reaction time and NCO content in the polyurethane synthesis
Conditions: molar ratio for NCO/OH or OH/OH: TDI/(TMP+PEG)=2/1; TMP/PEG=80/20; TDI/HPA=2/1; methanol, 1.5 ml; solid content 70%; polymerization temperature, 65°C; HPA was added at 3 h; methanol was added at 6 h

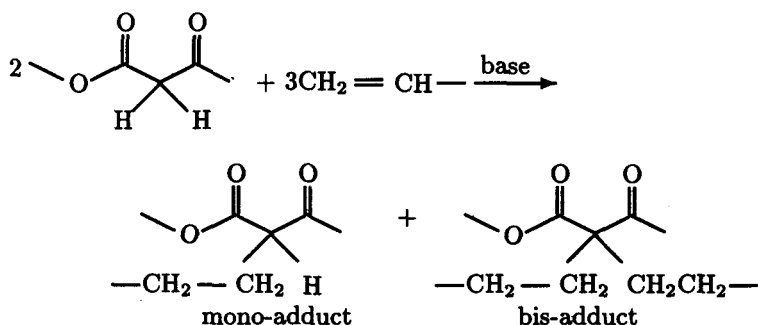
It was found that the actual solid content of different P(A) could all reach 70% regardless of the amount of BPO used. The molecular weight and the flowing viscosity decreased sharply with increasing the amount of BPO from 0.6 to 1.4 wt%. However, both of them changed slightly with further increasing to 1.8 wt%. So the most suitable amount of BPO was 1.4 wt%.

Different polyurethanes were synthesized with the change of the molecular weight of PEG. The relationship between the NCO content and the reaction time is shown

In Fig. 1. It was found that the reaction process is very similar for different systems. The NCO content decreases to a certain value in the first two stages during the 3 h reaction time and totally disappears when reacts for further 0.5 h after adding the methanol. Therefore, the reaction time should be fixed at 3 h, 3 h and 0.5 h for the three steps in the synthesis of P(U).

Study on Michael reaction between EAA and MA

The active methylene in acetoacetyl group consists of two active hydrogen atoms, which could react with vinylic groups to form mono- and bis-adducts via the Michael reaction catalyzed by a basic catalyst shown as the following:



A model Michael reaction between EAA and MA was performed to study the reaction mechanism and to learn about the reaction path way. The influence of reaction time on the composites was firstly studied under EAA/MA molar ratio of 1/1 and the results are shown in Fig.2. It could be seen that the reaction rates for EAA and MA are relatively the same and mono-adduct is formed as the main product at the first 4 h. After that, the rate for MA is higher than that for EAA and the yield of bis- adduct increases with decreasing the yield of mono-adduct slowly as prolonging reaction time until all MA exhausts at 29 h. These results indicate that the two active hydrogen atoms in acetoacetyl group could both participate in the Michael reaction and form mono- and bis- adducts stepwisely.

The influence of the molar ratio for EAA/MA on the composition of the reaction system has also been studied and the results are shown in Fig. 3. It can be seen that the total amount of the unreacted reactants could reach the lowest at EAA/MA molar ratio of 0.57—0.6/1. Additionally, higher yield of bis- adduct could be obtained at a lower EAA/MA molar ratio.

Properties of $P(A)/P(U)$ composite coatings

Two series of P(A)/P(U) composite coatings with different molar ratio of acetoacetyl/vinyl groups were prepared. Their crosslinking degree and mechanical properties were determined and summarized in Table 2. It was found that higher crosslinking degree and better performances could be obtained at the molar ratio of

0.6/1 of the reactive groups under different concentrations of DBU. These results are in accordance with the mechanism of the model reaction. Because at the molar ratio of 0.6/1, bis-adduct is formed as the main product, which means that the crosslinking structure between P(A) and P(U) is easier to form. So higher crosslinking degree and better mechanic performances are obtained under this condition.

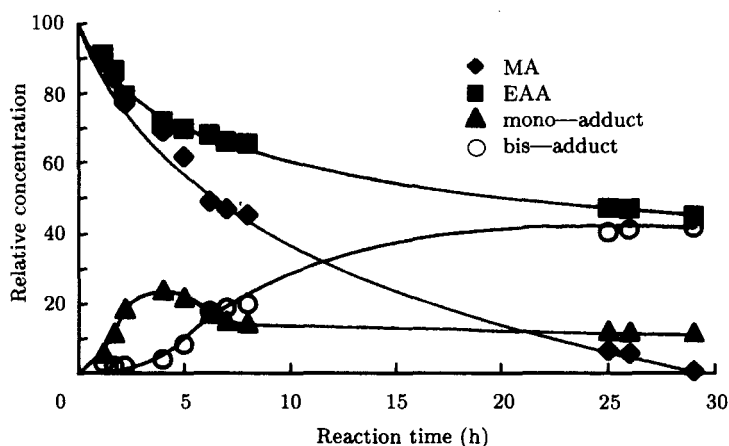


Fig. 2 The change of the relative concentration of different components with the reaction time

Conditions: EAA, 30 mmol; MA, 30 mmol; DBU, 2.4 mmol; o-dichlorobenzene, 10 mmol; solvent, toluene; reaction temperature, 25°C

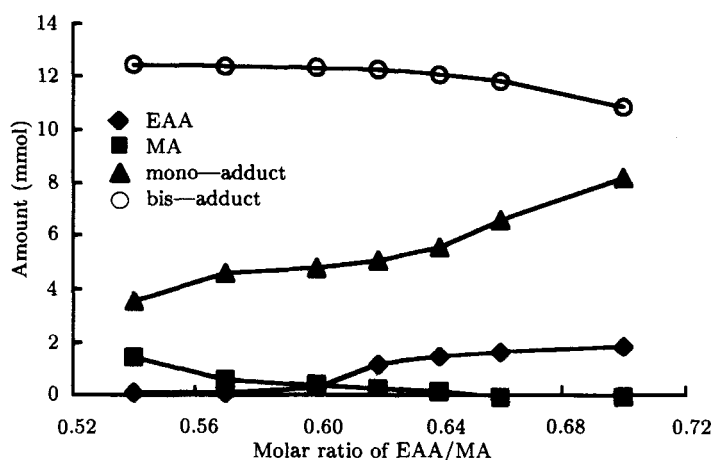


Fig. 3 Influence of the molar ratio of EAA/MA on the composition of the system

Conditions: MA, 30 mmol; reaction time, 56 h; others the same as Fig. 2

Table 3 shows the influence of the weight ratio of P(A) to P(U) on the properties of the composite coating under the molar ratio of 0.6/1 of the reactive groups. The results indicate that the crosslinking degree, impact strength, resistance to acid and

base remain the same for the different systems. However, the adhesion, hardness and solvent resistance are highly dependent on the weight ratio of P(A) to P(U). At higher content of P(A), the composite coating exhibits higher grade of adhesion. On the contrary, with increasing the content of P(U) in the composite coatings, better properties in hardness and solvent resistance are observed.

Table 2 Influence of molar ratio of the reactive groups on crosslinking degree and properties of the composite coatings

Molar ratio of the reactive groups	0.6/1				1/1			
[DBU] (v%)	10	25	35	50	10	25	35	50
Crosslinking degree (%)	46.2	83.1	93.0	93.1	19.1	57.5	87.3	88.9
Impact strength (kg-cm)	20	45	50	50	10	20	40	50
Hardness, pencil	B	H	3H	3H	B	HB	2H	2H
Adhesion, grade	1	1	1	1	1	1	1	1

Conditions: total P(A) and P(U), 2 g; DBU was diluted with toluene for preparing different concentrations, 0.025 ml for each sample.

Table 3 Effect of the weight ratio of P(A) to P(U) on the properties of the composite coating

Weight ratio of P(A) to P(U)	1.6/1 ^{a)}	0.8/1 ^{b)}	0.5/1 ^{c)}
Crosslinking degree (%)	88.1	90.1	91.9
Impact strength (kg-cm)	50	50	50
Acid resistance	no change	no change	no change
Base resistance	no change	no change	no change
Adhesion, grade	1	2	3
Hardness, pencil	2H	4H	6H
MEK rub resistance (times)	65	70	85

Conditions: molar ratio of functional groups, 0.6/1 DBU, 50v%, 0.04ml; MEK, methyl ethyl ketone; AAEM content in P(A): a) 10 wt%; b) 20 wt%; c) 30 wt%

Keywords:

Polyacrylate; Polyurethane; Composite coating; Crosslinking mechanism

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