

Preparation and Properties of UV curable urethane methacrylate oligomer

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Abstract

N,N-dihydroxyethyl methacrylamide (DHEMAA), which is a methacrylate modified by diol, has been prepared by reaction of diethylanol amine with methyl methacrylate. UV curable urethane methacrylate oligomers have been synthesized by the reaction of a series of diol, triol, DHEMAA and HEMA with TDI or IPDI in two reaction orders. The first reaction style is the TDI or IPDI reacted with HEMA first to give methacrylate group ending mono isocyanate, then the mono isocyanate reacted with diol or triol to generated urethane oligomer with two or more functional methacrylate groups. The secondary reaction style is the TDI or IPDI reacted with diol, triol or DHEMAA first to get oligomer, then resulted oligomer reacted with HEMA to obtain the UV curable product with multi-functional groups. The average molecular weight, structure unit of oligomer and number of functional groups could be tuned by adjusting of adding order, ratio of starting materials and the reaction condition. The UV curing properties such as curing rate, hardness of cured film, impact strength, flexibility and so on have been determined. The relationship between the component and the properties of cured film has been discussed.

Key words: Modified urethane methacrylate, UV curing, Double bond conversion, Mechanism properties

1. Introduction

Compared with thermal cure, UV curing technology possesses of the “5E” characteristic, which has widely used in electron encapsulation, the optical fiber coatings, the press-sensitive adhesive, the printing ink, the powder coating and so on, becoming an important green technology in the 21 century^[1]. UV curable materials mainly consist of the UV curable resin, the active dilute, photo-initiator, photosensitive and other functional additive. The UV curable resin, which has great effects on the properties of the final cured material such as the flexibility, the rigidity, and the adhesion etc., is one of the most important components in UV curable system. So far, the UV sensitive resins are mainly kinds of unsaturated polyester, polyester acrylate, the acrylate, polyether acrylate, acrylic polyurethane, epoxy acrylate and so on. Urethane acrylate oligomer has become an important UV curable resin in UV curable system^[2-5] due to polyurethane materials with the excellent wear resistance, high and low temperature resistance, better impact resistance etc. The preparation method of urethane oligomer and the raw

material strongly affect to the properties of final cured material. It is possible to obtain a material with novel properties by adjusting the structure of the polymer through different procedure and raw materials. It will be very important for development of new functional materials in UV curable field.

In this paper, N,N-dihydroxyethyl methacrylamide has been synthesized and a series of urethane methacrylate have been prepared by reaction of HEMA , DHEMAA, diol, and polyol with various kinds of isocyanate. The effects of the preparation condition and raw material on the properties of cured films have been investigated.

2. Experimental

The raw material and the apparatus

The diethylanol amine, β -hydroxyethyl methacrylate, methyl methacrylate(MMA) was obtained from Chemical Reagent Research Institute of Tianjin. The toluene diisocyanate (TDI) was from Tianjin Fangde Co., Ltd. The IPDI , photoinitiator 1173, were from Bayer Co. Ltd. Polyether diol was purchased from the Third Petrochemical Factory of Tianjin. The HDDA were obtained Tianjin Tianjiao Chemical Co., Ltd. The benzophenone was obtained from Shanghai First Regent Factory.

FT-IR spectra of the samples were recorded on a Bruker Vector-22 spectrometer. The DPC analysis was accomplished by using the DPC system of DSC 2910, and analyses with TA Universal Analysis. The UV curing tests were carried out on F300+LC-6B UV curing system (Fusion UV System Co., Ltd., USA), The pencil hardness, impact strength, flexibility of cured films were determined by QCJ paint film impinge, QTX paint film elasticity recognizer, respectively made by Tianjin Zhongya Material Tester Factory.

The preparation of N, N-dihydroxyethyl methacrylamide (DHEMAA)

Typical procedure: To a 4-neck flask equipped with mechanical agitator, thermometer and fractionating tube, calculated amount of methyl methacrylate, diethylanolamine, inhibitor and catalyst were added. The reaction was carried out under reflux and the byproduct (methanol) was separated out by fractionation. After 4 hours, the unreacted methyl methacrylate was distilled under vacuum to give light yellow oil (which is the mixture of N, N-dihydroxyethyl methacrylamide (**DHEMAA**) and amine substituted propionic ester). The byproduct of amine substituted propionic ester **b** can be separated by washing the product with acidic water. The DHEMAA with different amount of **b** can be obtained by adjusting the reaction and separation condition or mixing of pure DHEMAA and **b**.

The preparation of urethane methacrylate

Procedure A:

Typical procedure: According to the formulation, the calculated amount of β -hydroxyethyl methacrylate with the inhibitor (0.5% in total weight) was added dropwise to isocyanate TDI (or IPDI)

with DBT(1% in total weight) in a 4-necked flask equipped with mechanical agitator, thermometer, adding tube and condenser. After adding, the reaction temperature was kept at about 40°C for 2-3h to give monoisocyanate with methacrylate as end group. Then the calculated amount of mixture of diol and polyol was added slowly. The reaction mixture was heated up tardily to 80°C, and kept the reaction going for 4h ~ 5h till the residual NCO being about 0.5% by chemical titration. Due to the high viscosity of the mixture, some amount of HDDA was added to make the dilute solution, which was marked as PUA-A series of oligomer. The samples numbered as PUA-A-1 to PUA-A-6 are prepared by reaction of monoisocyanate ending methacrylate with the mixture of N,N-dihydroxyethyl methylacrylamide (the content of **b** is 2%) and polyether diol in the weight ratio of 0:6, 1:5, 2:4, 3:3, 4:2, and 1:1, then diluted by 50wt% of HDDA, respectively. The samples numbered as PUA-A-7 to PUA-A-10 are prepared in similar way by reaction of monoisocyanate ending methacrylate with the mixture of polyether diol and N,N-dihydroxyethyl methylacrylamide in the weight ratio of 1:1, in which the content of tertiary amine **b** is 3% , 5% , 7% and 10%, and then diluted by 50wt% of HDDA. The samples numbered as PUA-A-11 to PUA-A-13 are prepared in similar way , but using IPDI to replace TDI, with the mixture of N,N-dihydroxyethyl methylacrylamide (the content of tertiary amine **b** is 2%) and polyether diol in the weight ratio of 1:5, 2:4 and 3:3, then diluted by 50wt% of HDDA.

Procedure B :

Typical procedure: According to the formulation, the calculated amount of mixture of diol and polyol with the inhibitor (0.5% in total weight) was added dropwise to isocyanate TDI with DBT(1% in total weight) in a 4-necked flask equipped with mechanical agitator, thermometer, adding tube and condenser. After adding, the reaction temperature was kept at about 40°C for 2-3h to produce polyurethane oligomer with desired value of NCO, which determined by chemical titration. Then the calculated amount of β -hydroxyethyl methacrylate with inhibitor (0.5% in total weight) was added. The reaction mixture was warming up slowly to 80°C, and kept the reaction running for 4h ~ 5h till the residual NCO being about 0.5% by chemical titration. Some amount of HDDA was added to make the dilute solution, which was marked as PUA-B series of oligomer. The samples numbered as PUA-B-2 to PUA-B-6 are prepared according to the procedure described above by the reaction of TDI with the mixture of N,N-dihydroxyethyl methylacrylamide (the content of tertiary amine **b** is 2%) and

polyether diol in the weight ratio of 1:5, 2:4, 3:3, 4:2, and 1:1, then reacted with β -hydroxyethyl methacrylate, following by diluted with 50wt% of HDDA, respectively.

Preparation of UV curable samples and UV curing

All UV curable samples were prepared by adding 1wt% of photoinitiator 1173 and 1% of benzophenone to above modified PUA solution.

All samples were coated on the glass surface or tinplate by plate coater or the coil painter with 100 μ m at room temperature, then cured by F300+LC-6B UV curing system under expose of lamp D with curing energy of 740mJ/cm² at the transmit rate of 6m/min. Curing time was measured by finger-press method.

Test method

The samples on the glass plate are used to test the hardness, curing time and other properties, the samples on the tinplate plate are used to test the toughness and impact strength. The pencil hardness was tested by pencil scratch durometer referred to GB6739-86. The impact strength was determined by heavy hammer fall test according to GB1732-79, observed the film by four times magnifier and checked the film whether there are some damages such as reticulate pattern, crack and abscission etc. The toughness was determined by film toughness tester referred to GBPT1731 - 93 by bending the tinplate with cured sample on the axis stick with different diameters (millimeter), observed the film by four times magnifier and checked the film if there are the reticulate pattern, crack and abscission etc. The gel fraction of cured film is calculated base on the following equation: Gel% = $(m_2 / m_1) \times 100$, where m_1 is the weight of sample before immerge into acetone, m_2 is the weight of the dry sample after immerge in the acetone for 48 hours (The sample was took out from the acetone solution and wiped to dry, vacuum dry until constant weight).

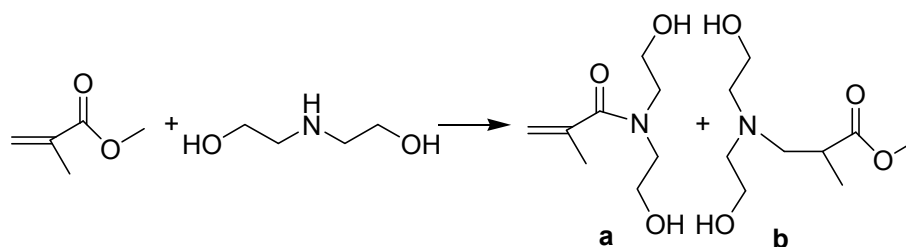
3. Results and the discuss

Preparation of monomer

UV curing material, which consists of some polyurethane acrylate (PUA), has the advantage of both polyurethane and polyacrylate. But the curing rate of regular PUA is relatively slow and the price is high.

Because the properties of polyurethane can be easily tuned by adjusting the ratio of different raw material and preparation procedure, it is possible to prepare some novel polyurethane with unique properties, such as higher UV curing rate, better flexibility and so on. As we know, the amine is a kind of activator of UV curing component. But amine with low molecular weight can easily migrate to surface and make the material aged. Moreover, the small molecular amine is also toxic. It is very

important to prepare polymeric amine or the polyurethane molecular containing amine group. Based on this consideration, the diol with methacrylate and amine functional groups have been prepared as shown in scheme 1.



Scheme 1 Synthesis process of N,N-dihydroxyethyl methacrylamide

Fig. 1 showed the IR spectrum of the compound, the signals at 3385 , 1733 , 1617 , 1296 cm^{-1} are responded to the N-H asymmetry stretching vibration on the CO-N-H , C=O symmetry stretching vibration ,C=O symmetry stretching vibration on the CO-N-H and C-N-H curving vibration, respectively, which confirmed the amidation reaction occurred. In addition, the Michael addition of amine to methacrylate formed a diol containing tertiary amine without double bond. Due to the Michael addition and ester exchange reaction are in the equilibrium at high temperature, the ratio of the two products can be tuned. N,N-dihydroxyethyl methacrylamide with different amount of tertiary amine can be obtained by controlling the reaction condition and catalyst or separations . The content of tertiary amine is determined by acid-base titration.

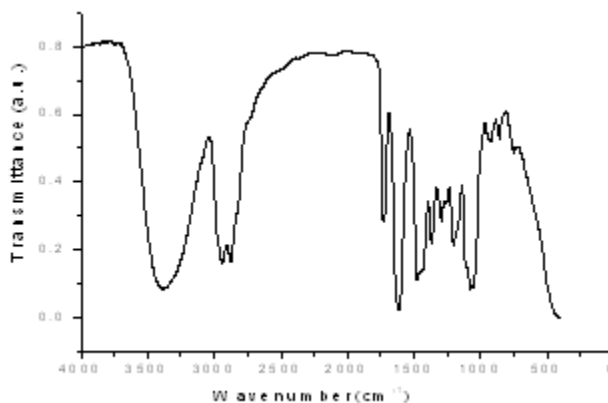


Fig .1 the infrared spectrogram of the product 1

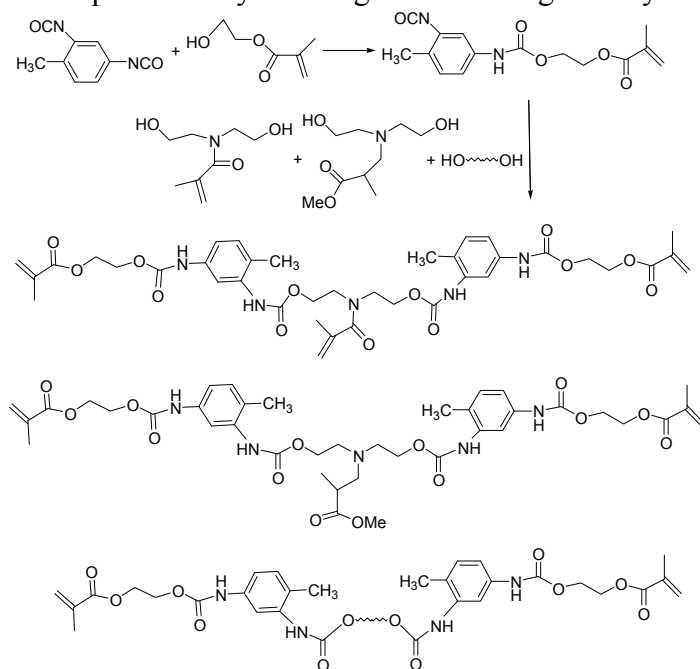
Preparation of polyurethane methacrylate

The polyurethane methacrylates are generally prepared by the reaction of diisocyanate with an equivalent hydroxyethyl methacrylate at lower temperature to make a methacrylate ending monoisocyanate, and then this intermediate would react with saturated or unsaturated multi-hydroxyl compound [6]. The mechanical properties of the film obtained by crossing of polyurethane methacrylate oligomer are obviously depended on the saturated or unsaturated multi-hydroxyl component. Generally,

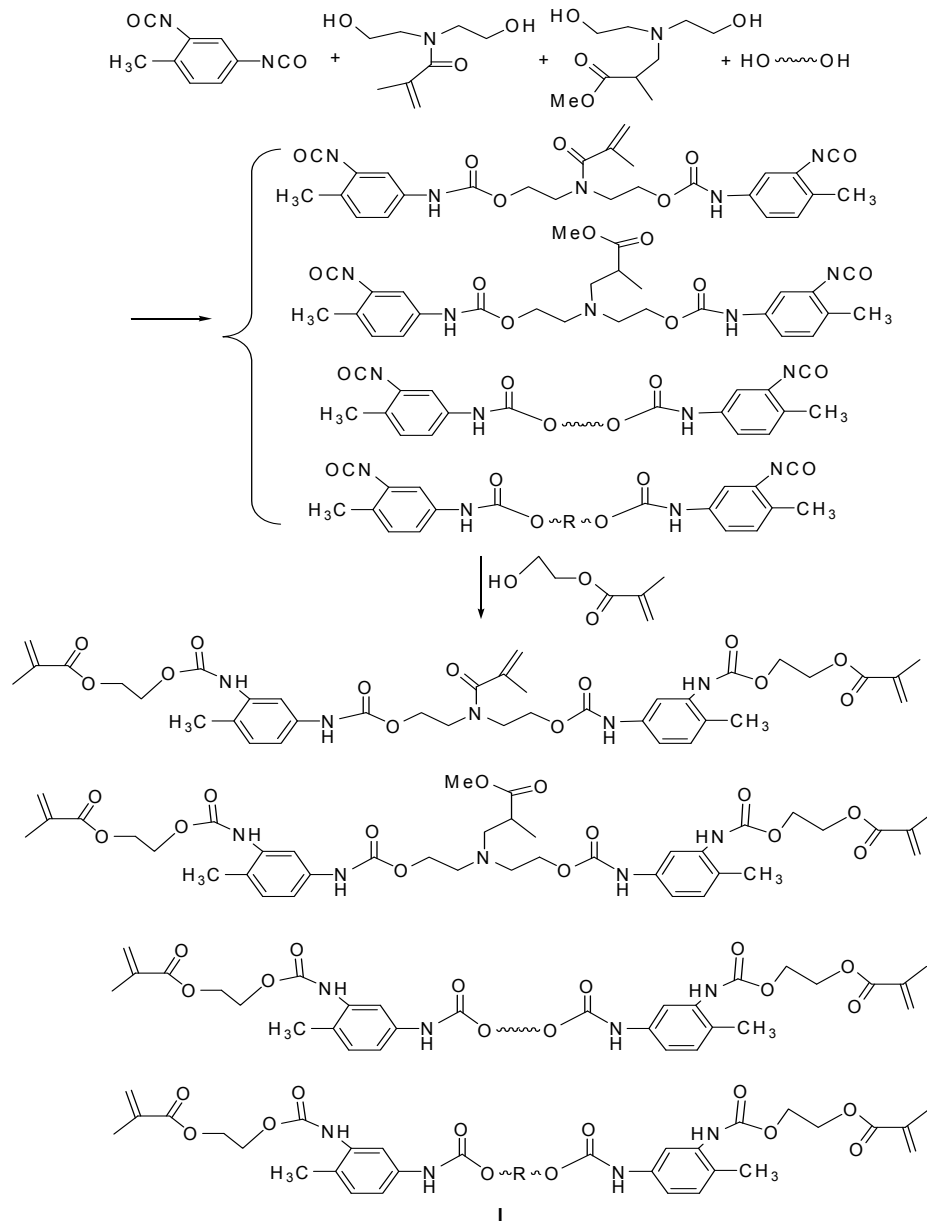
multi functional methacrylate groups are from the reaction of methacrylate ending monoisocyanate with polyol, but if the methacrylate ending monoisocyanate from the above procedure containing more unreacted diisocyanate, the polyol might make the whole reaction system crosslinked.

Here, the polyurethane methacrylate can be prepared in two ways as described in Scheme 2 and 3.

In pathway A, the β -hydroxyethyl methacrylate reacted with isocyanate TDI (or IPDI) to give monoisocyanate with methacrylate as end group. Then the intermediate reacted with diol and polyol to generate the polyurethane methacrylate. In pathway B, the adding order is reversed, which may make the system more complex than the pathway A. The viscosity of the product is greatly affected by the different pathway way. The viscosity of oligomer prepared by procedure A is lower than that by procedure B, because diisocyanate only reacts with mono alcohol to make monoisocyanate and then reacts with diol or multi-hydroxyl, the chain-extending reaction is impossible to occur, the average molecular weight of the oligomer is lower. In the pathway B, diisocyanate reacts with diol or polyol, the structure of the polymer is relatively more complex, and the chain-extending reaction make the oligomer with higher molecular weight. The reactions are the same for both TDI and IPDI. The functionality of polyurethane modified oligomer can be increased by changing the ratio of isocyanate and various diols (in which diol with methacrylate can be used to adjust the functionality of system instead of polyol) to adjust the cured rate and various properties of UV curing component. The FTIR of polyurethane methacrylate of PUA-A-1 is shown in Fig.2. Due to N,N-dihydroxyethyl methylacrylamide component with some amount of diol with tertiary amine, so this active amine would be blocked in the oligomer chain. In this way, the obtained product may have higher UV curing activity [7].



Scheme 2 The chemical reaction in pathway A



Scheme 3 The chemical reaction in pathway B

Effects of the reaction conditions

Temperature is one of the important factors for the reaction rate, and selectivity. The activity of contrapuntal NCO of the TDI is higher than that of the adjacent one. Owing to the steric effect, the activity of NCO of IPDI molecule at primary carbon is higher than that at secondary carbon. The reaction is exothermic; so the reaction was carried out at low temperature in order to increase the selectivity. the reactive temperature for the first step was kept at about 20 ~ 40°C. In the second step the reactive temperature was controlled at 80 ~ 90°C for lower viscosity and higher reaction rate. If the

temperature is too high, the NCO would react with less active hydrogen at amide, which make the whole reaction system viscous, even crosslink to be an insoluble gel. In fact, these side reactions not only affect the viscosity of resin, but also result in the poor properties of UV curing material.

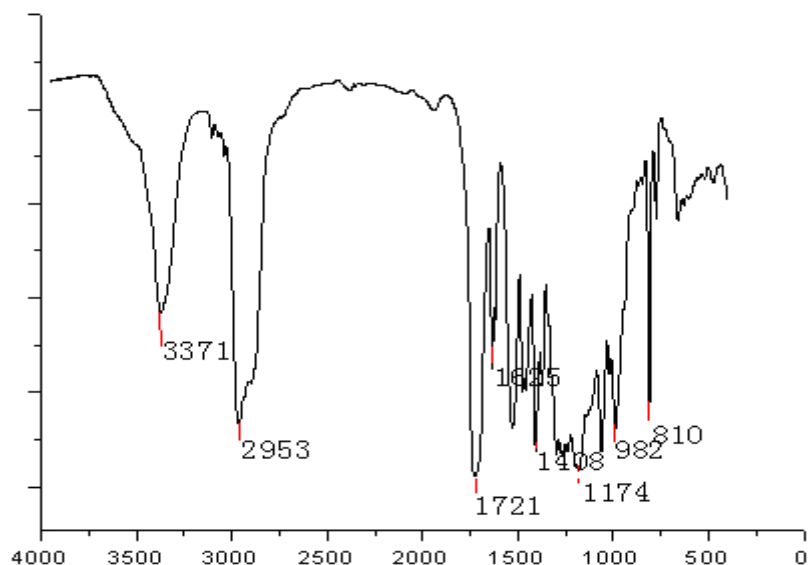


Fig. 2 FTIR spectrum of PUA-A-1

Properties to UV curing system

UV curing rate

The curing rate of UV curing component were shown in Fig.3. According to the Fig.3, in the series of PUA-A(1-6) , the curing rate of the general polyurethane acrylate PUA-A-1 is much lower than that of PUA-A(2-6) made by N,N-dihydroxyethyl methylacrylamide as part of diols . This result might be due to the PUA-A (2-6) with higher functionality (methacrylate groups) and containing some active amine. The curing rate increases as the amount of the N,N-dihydroxyethyl methylacrylamide. This tendency was similar in the series of PUA-B and PUA-A (11-13). When the IPDI is used to instead of TDI, the curing rate was slightly slow. It was worth to point out the amine could increase the curing rate more effectively. The effect of amine on the curing rate was large than that of functional group of methacrylate. Because the UV-curing speed determined by method of the finger-press was not so accurate, the DPC technology was used to track the UV-curing process of PUA. The results were shown in Fig. 4-5 separately. From Fig. 4, it was clearly shown that the curing rate of PUA-A-1 was indeed slower than that of modified PUA-A (2-6). The tendency was similar to the result obtained from the method of the finger-press. The curing rate increased as the amount of N, N-dihydroxyethyl methylacrylamide increase .Similar results of curing rate were observed when IPDI was used to instead of TDI (Fig. 5).

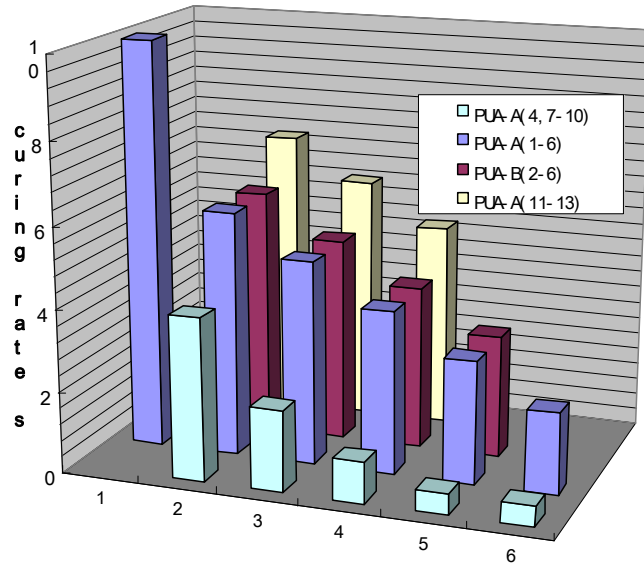


Fig.3 UV curing rate of different UV curable PUA
 (The abscissa showed the different numbers, the ordinate showed the different series.)

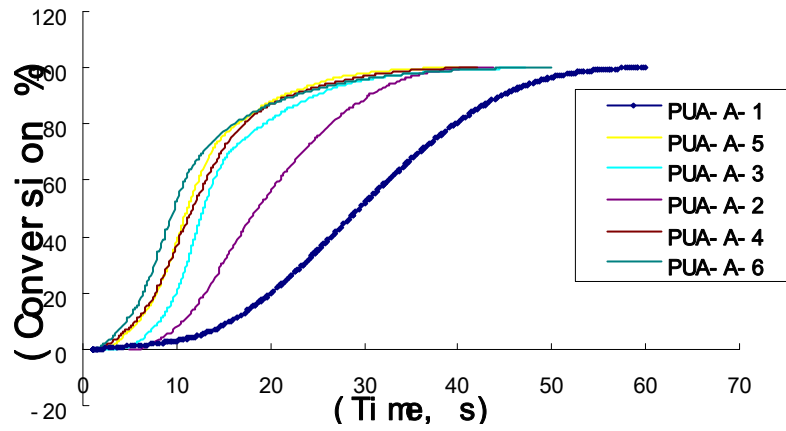


Fig.4 UV curing progress of the PUA-A-(1-6) traced by DPC

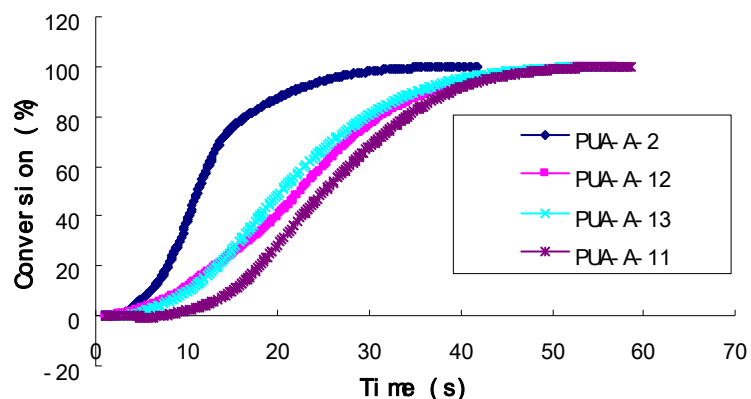


Fig.5 UV curing progress of the PUA-A-(2,11 –13) samples traced by DPC

In order to further investigating UV curing progress of PUA-A-2 sample, the curing process was also traced by FTIR, and shown in Fig.6. The FTIR spectra were recorded after the sample cured by UV for different time (The curing process was carried out in F300+LC-6B UV curing system). The absorption peaks at 812 cm^{-1} and 1636 cm^{-1} are the characteristic absorption peaks of polyurethane methacrylate. As the curing degree increasing, these two peaks would decrease. The UV curing degree is generally determined based on this variation. From Fig. 6, the whole curing reaction was not complete after irradiated 4s. The signal of carbonyl shifts toward the red side due to the polymerization of the double bond of methacrylate to form saturated ester.

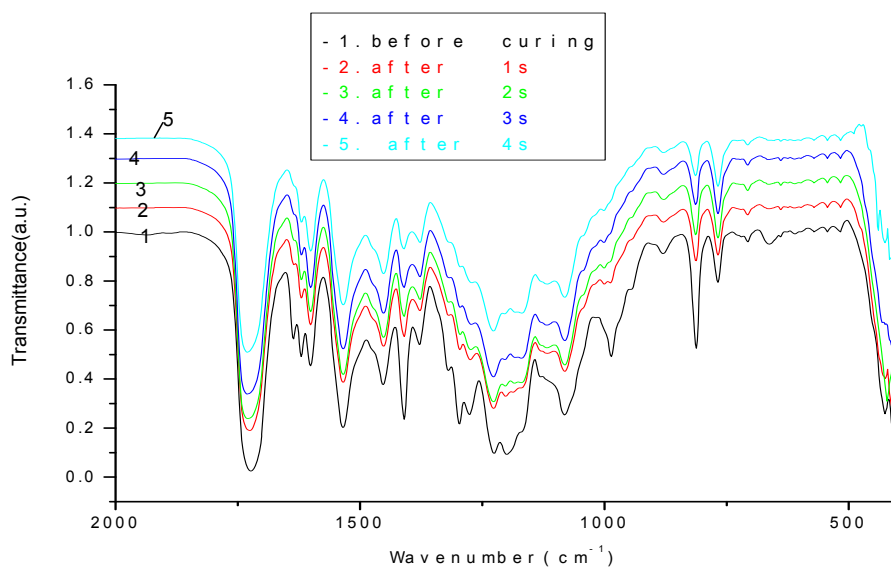


Fig. 6 Infrared spectra of PUA-A-2 at different curing time

The impact strengthen of the UV cured film

The impact strengthen of the UV cured film is an important factor for the material application. The impact strengthen of cured film obtained were shown in Fig.7. It decreased as the numbers of functionality group increase, which might be due to higher cross-link density. According to Fig.7, this trend only related to the UV curable component, and did not relate to the preparation procedure. The impact strength of PUA-A (11-13) prepared by IPDI was better than that prepared by TDI. As the concentration of active amine in the curing system increased, the curing rate would increase largely, which would result in higher cross-link density and nonuniformity. In this way the impact strength of material would decrease.

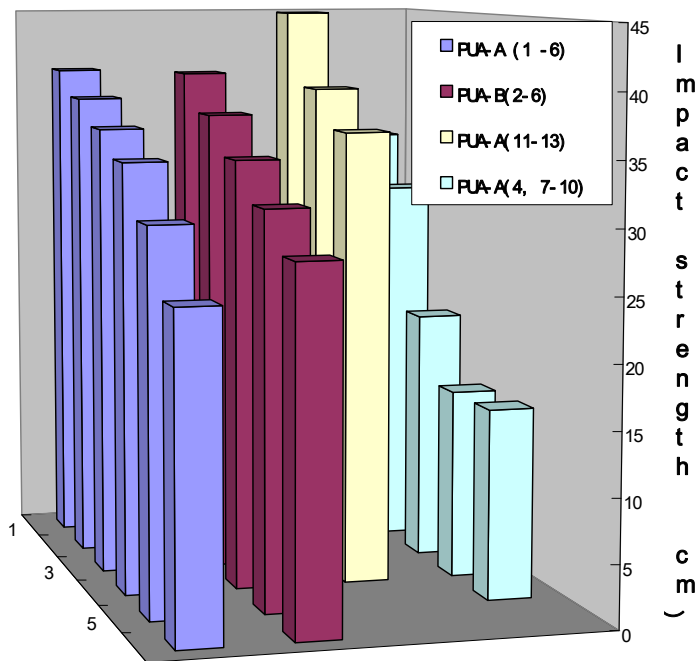


Fig.7 The impact strength of the UV cured film

The hardness of the UV cured film

The pencil hardness of UV cured film was shown in Fig.8. The hardness of cured film increased as the numbers of functionality group increase. The pencil hardness of film obtained by PUA-A was higher than that from PUA-B. The hardness of the film would increase with the effective concentration of active amine. At similar condition, the hardness of film obtained from IPDI modified PUA was higher than that from TDI.

The flexibility of the UV cured film

The flexibility is also an important factor of film. Fig.9 showed the film flexibility of UV cured PUA. The film flexibility of UV curing formulation prepared by procedure A fell down as the number of effective functionality group increase. Although this tendency was also observed in PUA-B series, the

decrease rate was slower than that of PUA-A. The film flexibility of PUA-A (11-13) prepared by IPDI was better than that of PUA-A (2-4) prepared by TDI.

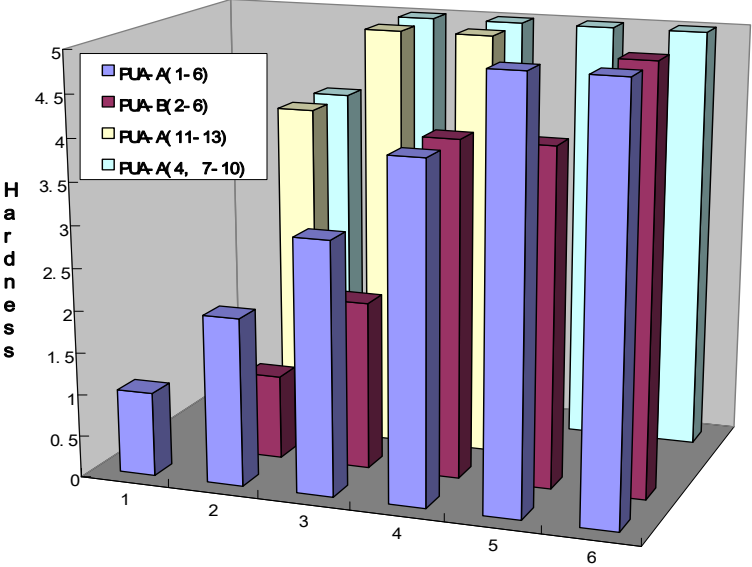


Fig.8 The pencil hardness of the UV cured film

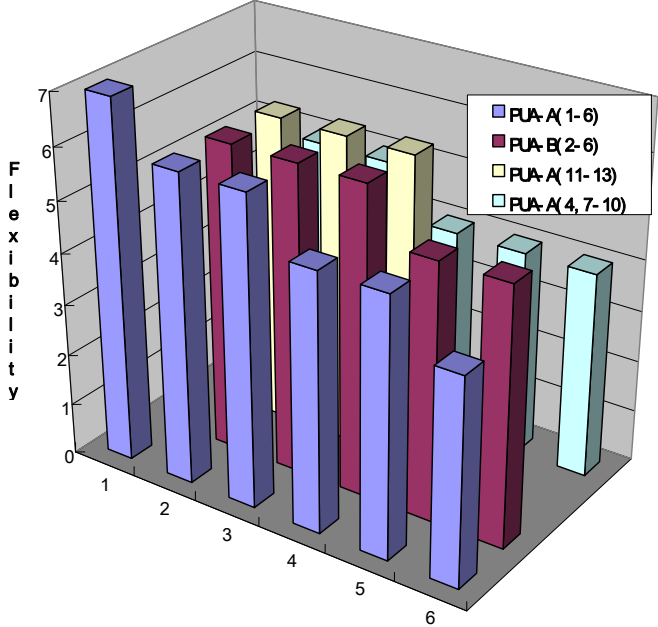


Fig.9 The flexibility of the UV cured film

The gel fraction of the UV cured film

The gel fraction of the UV cured film can reveal UV cured degree and the film's solvent resistance in certain degree. The gel fraction of the UV cured film was shown in Fig.10. As we known, the reaction degree increased as the number of effective functional group increase, but as the number increased, the reaction went so fast that the cross-link gel forms quickly, which limited the movement of unreacted monomer, resulted the slower reaction rate. The cross-linked gel might contain some unreacted monomer, which would decrease the gel fraction. So we can explain the gel fraction being increase first and then decrease as increase of the number of the functional group. For the active amine, the tendency of gel fraction was almost the same. The gel fraction increased at first and then decreased as the amount of amine increase.

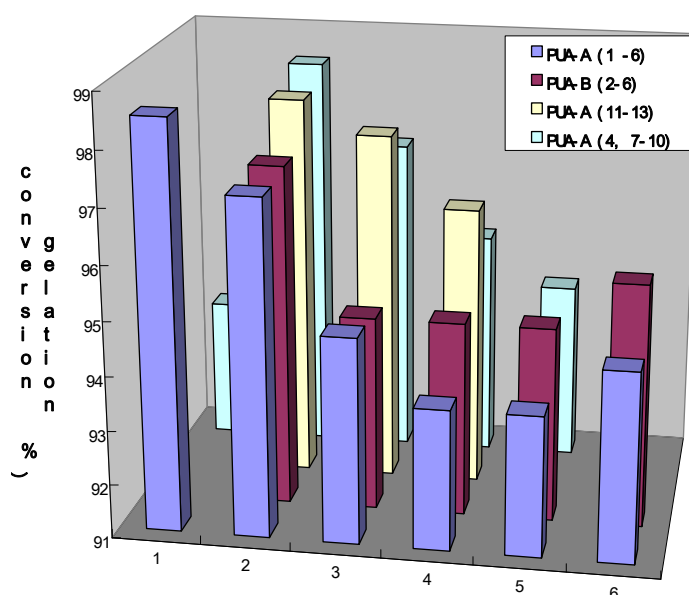


Fig.10 The gel fraction of the UV cured film(the cross linking density)

The film obtained by UV cured of PUA-A(11-13), which was made from IPDI, was almost colorless. While the film from PUA-A made from TDI showed some degree of yellowing after UV cured. The color of the film increased as the increase of active amine.

Conclusions

N,N-dihydroxyethyl methacrylamide (DHEMAA) prepared by reaction of diethylanol amine with methyl methacrylate has been used as functional diol to make functional polyurethane methacrylate. The composition and the structure of UV curable urethane methacrylate oligomers can be tuned by adjusting

the ratio of different raw metrical and the procedure. The UV curing rate can be increase by increase the amount of DHEMAA or amine **b**. The cured films with good performance can prepare by adjusting the mixing composition.

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