

Cardanol-based branched UV-cured acrylic oligomers

Ren Liu Junchao Zheng Jijia Zhu Xiaoya Liu

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

Abstract

A series of novel biobased UV-curable resins, multi-arms acrylates (BMAs) were synthesized from renewable cardanol and bio-polyols, such as glycerol, xylitol, tripolyglycerol and sucrose. The resulting UV-curable resins, containing about 55wt % biorenewable content, have varying arms of cardanol from 3 to 6 by changing the kind of biobased polyol core. All of the resins cured rapidly and formed rigid coatings with a high degree of conversion. Coated film properties of pendulum hardness, flexibility and adhesion of the cross-linked resins were investigated. Mechanical properties and thermal properties of the cured films were also evaluated. The results showed that mechanical properties and thermal stability of BMAs films were excellent, it indicating that BMAs could produce UV-curable coatings of balanced coating performance with reasonably high biorenewable content.

Keywords: Bio-base; UV-curable coatings; Renewable resources; Multi-arm acrylates

1. Introduction

In recent years, UV-curable coatings have received considerable attention, due to their advantages such as lower energy consumption, less environmental pollution, lower process costs, high chemical stability, and very rapid curing even at ambient temperatures^[1-3]. However, with the continuous depletion of fossil oils, dramatic fluctuations in the price of oil and environmental concerns, there is an urgent need to reduce the amount of petroleum consumed in the coating industry^[4-5].

Greater attention has been paid to the utilization of renewable raw materials in both industrial and academic settings, due to concerns regarding environmental sustainability^[6-7]. The utilization of renewable raw materials in coatings can meet some principles of green chemistry, such as a built-in design for degradation or an expected lower toxicity^[8]. Combination of the advantages of both renewable raw materials and UV curing technology in the coating industry is a topic of great interest

[9-12]

Among the renewable resources, Cardanol, obtained from Cashew Nut Shell Liquid (CNSL), is unique in that it contains a phenolic moiety with an unsaturated C₁₅ side chain. This combination offers a wide variety of possibilities for the synthetic chemist^[13-15]. Considerable attention from polymer scientists is devoted to utilize their potential attributes as a substitute for petrochemical derivatives. Of late cardanol and its derivatives have been used in the preparation of surface coatings, adhesives and other epoxy applications^[16-18].

Polyol is one of the essential raw materials (monomers) in the production of polyurethanes used in adhesives, coatings, building insulation, and flexible or rigid foams. However, polyols are most produced from petroleum. With the worldwide demands for replacing petroleum derived raw materials from renewable, bio-based polyols in the production of valuable polymeric materials are quite significant from both a social and an environmental viewpoint. Bio-based polyols have been currently used in preparation of hyperbranched acrylates, epoxy resins, and waterborne polyurethane dispersions^[19-22].

But the preparation of UV-curable multi-arms acrylates from cardanol and bio-based polyols has not been reported yet in the past researches. In the present study, a novel kind of degree of functionality multi-arms acrylates based on bio-based polyols core (BMAs) were prepared and characterized by epoxy value, FTIR, ¹H-NMR and GPC. The cure kinetics of BMAs based formulations and the final UV cured films properties were investigated and discussed in this contribution.

2. Experimental

2.1 Synthesis of acrylated three-arm oligomer based on core glycerol

All samples of multi-arms acrylates based on polyols core were synthesized according to the same general procedure as described for three-arms acrylates based on glycerol core (BMAs-3) below. Products were named BMAs-3, BMAs-4, BMAs-5 and BMAs-6 corresponding to glycerol, xylitol, tripilyglycerol and sucrose as the core polyols.

Three-arm oligomer based on core glycerol was achieved via reaction of glycerol,

ECD and MHHPA. In a three neck round bottom flask fitted with a mechanical stirrer, dropping funnel and condenser, glycerol and TPP were taken. The reaction mixture was stirred at 95°C while MHHPA was dropped into the flask over a period of 60min. The reacting mixture was stirred until the acid value reduced to half of the initial value. The acid value of the oligomer is 175.3 mg KOH/g as determined by titration according to a literature procedure [23]. After that, ECD was dropped into the flask over a period of 60min. The reaction mixture was stirred at 100°C until the acid value reached below five.

Epoxidized three-arm oligomer was prepared by reaction of the unsaturation sites of the three-arm oligomer with chloroperbenzoic acid according to a literature procedure [24]. The mixture of three-arm oligomer and MCPBA was taken in a round bottom flask, diluting with 200ml of dichloromethane. The reaction mixture was cooled in an ice bath to 0~5°C and stirred for 3 h. The solution was filtered, washed with a water solution of Na₂CO₃, and dried. The product obtained is epoxidized three-arm oligomer.

To introduce the acrylate functional group, the epoxidized three-arm oligomer is reacted with acrylic acid to form acrylated three-arm oligomer. Epoxidized three-arm oligomer, TPP and MEHQ were mixed in a three-neck round bottom flask equipped with a mechanical stirrer, dropping funnel and condenser. The reaction mixture was stirred at 105°C while AA was dropped into the flask for 0.5h. The reactions were performed until the acid value reached below five, and then a clear, yellow, viscous three-arm acrylate (BMAs-3) was obtained.

2.2 Preparation of cured coatings

The UV-curable coatings were formulated by mixing photosensitive oligomers and 3wt% photoinitiators (Irgacure 184/TPO = 2.5:0.5w/w). The obtained mixtures were homogenized and coated on aluminum panels (7.6 cm×15 cm from Q-panel) and glass substrate by means of a BYK spreader obtaining uniform thick films (30µm thickness). The wet thin films were cured by exposure to an F300 UVA lamp (1 kW, Fusion UV systems, USA) with the band conveyor speed of 5.0 in./min for 2 passes.

The total incident light intensity was 1600mJ/cm², determined using a UV-Integrator 140 power meter.

2.3 Characterization

König hardness was the testing mode (ASTM D 4366), with the values reported in seconds (s). Pencil hardness was measured using ASTM D 3363. Adhesion test was performed using the standard crosshatch adhesion test (ASTM D 3359). T blend test was also used to determine the flexibility of the coatings (GB12754). A gloss-meter (Gloss checker JKG 2-60°, Tianjing JingkeMaterials Testing Co., China) was used to analyze the surface glossinessfilms bymeasuring the 60° glossiness of each film according to ASTM D523. Contact angles were measured using a DATA physics OCA40 contact angle goniometer equipped with an environmental chamber. The tensile tests were carried out at 25 °C using an electronic universal testing machine (WDT-10) with a crosshead speed of 5 mm/min. Thermogravimetric analysis (TGA) was performed on cured samples (about 10mg) using a Mettler Toledo STAR thermogravimetric analyzer, with a heating rate of 15°C/min from 25 to 650 °C. Nitrogen was used as the purge gas at a 50 mL/min flow rate.

3. Results and Discussion

3.1 Characterization of BMAs

Table.1 Biorenewable contents, acrylate functionality and molecular weight of BPMAs

Sample	BRC (%)	Acrylate functionality	Acrylate equivalent (grams/mol)	M _{theor} (g/mol)	GPC	
					Mn (g/mol)	PDI
BMA _s -3	57.9	6	365.3	2192	2332	1.41
BMA _s -4	55.0	8	369.0	2952	3252	1.36
BMA _s -5	55.9	10	374.0	3740	3792	1.53
BMA _s -6	56.1	12	378.5	4542	4492	1.68

The biorenewable content, acrylate functionality, molecular weight and molecular weight distribution of synthesized BMAs are given in Table 1. The United States Department of Agriculture defines the biobased content of a product as

the “amount of biobased carbon in the material or product as a percent of the weight (mass) of the total organic carbon in the product”, the biobased content can be calculated by the equation ^[20]:

$$\%BRC = 100 \times \frac{\text{Biorenewable Carbon Atoms}}{\text{Total Carbon Atoms}}$$

The biobased contents of BMAs can reach near to 60%, respectively. Acrylate equivalent and molecular weight of BMAs were found to increase with increasing of arms within the range studied, since the more arms of BMAs has higher molecular weight and more acrylate functionality.

3.2 Coating Properties

Table 2 Properties of UV curable coatings

Sample	Pendulum hardness (sec)	Pencil hardness	Cross-hatch adhesion / level	T blend /T	Gloss /60°
BMA _s -3	109	2H	0	0	114
BMA _s -4	104	2H	0	0	115
BMA _s -5	107	3H	0	0	120
BMA _s -6	111	3H	0	0	123

The coating physical properties were tested. Table 2 shows the coating pendulum hardness, flexibility and adhesion respectively. The results indicate that the pendulum hardness of BMAs coatings could reach close to 110, and pencil hardness increased from 2H to 3H with the increasing the arms of BMAs. And the same time, the flexibility of BMAs film show good results. Consequently compromise between the hardness and flexibility can be achieved, which is attributed to the rigid molecular structure and flexible aliphatic chain of cardanol. The Adhesion of coatings was excellent because the BMAs contain a lot of polar groups, and the Gloss of coatings is around 120. Therefore, it can be seen that the BMAs coatings have excellent balanced properties.

3.3 Light transmittance

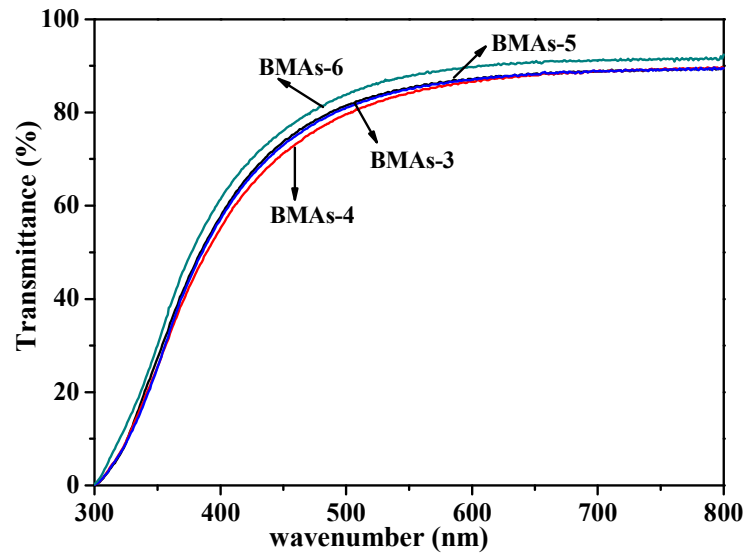


Fig.1 UV-visible spectrum of BMAs cured films

The transparency of coatings was evaluated by UV-visible measurement (Fig.1). The transmittance of the cured films was approach 90% in the range of visible wavelengths. The BMAs cured films show excellent transparency.

3.4 Water absorption and gel content

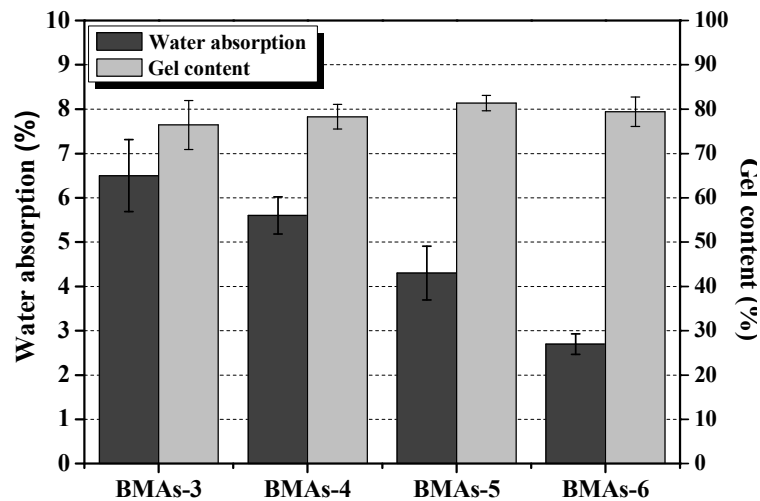


Fig.2 Water absorption and gel content of BMAs cured films

The result of water absorption as displayed in Fig.2 shows that water absorption decreased from 6.5 to 2.7% with the arms of resins increased. Gel content refers to the percentage of cross-linking that occurs in the coatings film. From result given in Fig.2, gel content was found to increase from 76.3 to 79.6% with the increasing arms of

BMA_s, which is due to increasing of crosslink density.

3.5 Water contact angle and stability in water of coatings

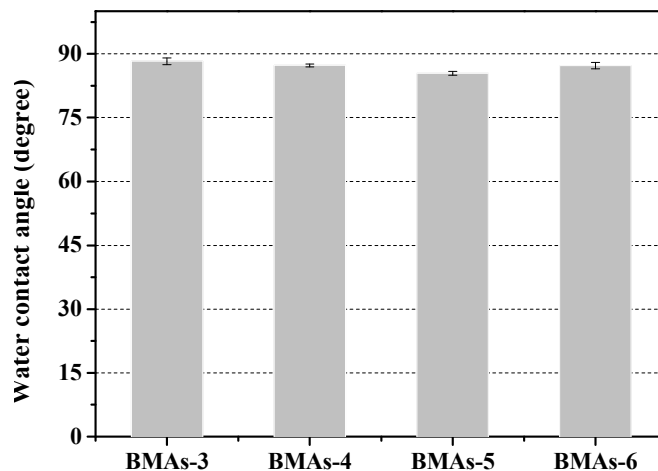


Fig.3 Water contact angle of BMA_s coatings.

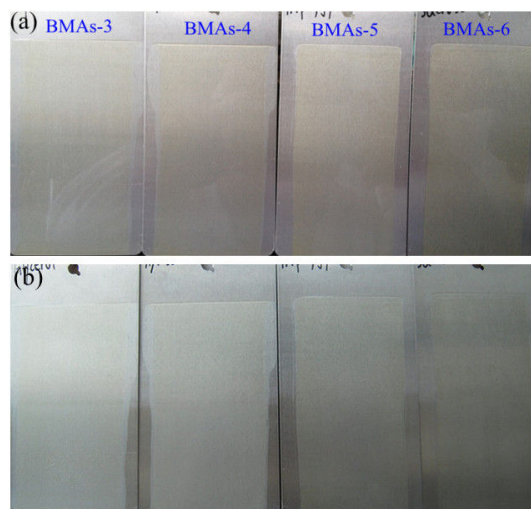


Fig.4 Coating film images (a) before and (b) after 7 days tap water immersion

The water contact angle of the BMA_s coatings was determined to understand the relative hydrophilicity/ hydrophobicity of the coatings surfaces. Fig.3 shows a plot of water contact angle of the coatings. The difference between the BMA_s films is negligible, indicating that the number of arms and the kind of core polyols do not have a significant effect on the water contact angle of the BMA_s coatings. Results of the contact angle measurements correlated well with the results of water immersion test of the coatings shown in Fig.4. Coating films showed rather good stability in water and well adhered to the bare aluminum panel, after 7 days water immersion. The results of contact angle and stability in water experiments suggest that type of

biobased polyols as well as the number of arms in BMAs resins not influenced the relative hydrophilicity of the coatings.

3.6 Tensile Properties of coatings

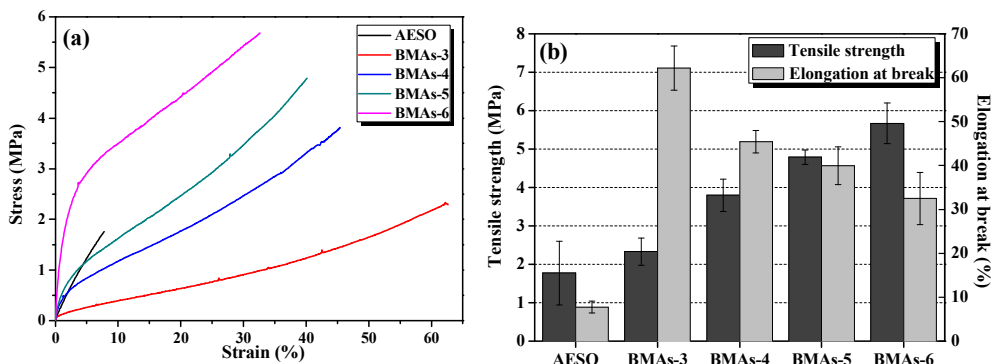


Fig.5 (a) Typical stress strain curves and (b) tensile strength and elongation of cured films

The stress–strain curves of UV cured films are shown in Fig.5 (a). The tensile modulus and elongation at break were obtained and the results were shown in Fig.5 (b). As the number of BMAs arms increased, the rigidity of the coating film increased, resulting in the increase of tensile modulus and the decrease of elongation at break, these are in good agreement with the coating properties.

3.7 Thermal behavior characterization of coatings

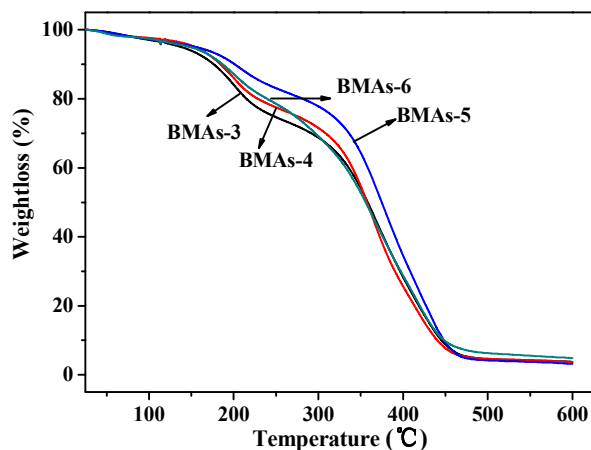


Fig.6 TGA of BMAs cured films

TGA was performed on the coatings to determine their thermal stability. Results of TGA are shown in Fig.6. In general, the coatings showed good thermal stability. The onset temperature for the degradation of the coatings was around 200° C.

4. Conclusions

A series of bio-based multi-arms acrylates (BMAs) derived from glycerol, xylitol, tripolyglycerol, sucrose and cardanol was prepared in simple, three-stage process. These resins were used as oligomers in UV curable compositions. Coatings obtained from these BMAs exhibit good hardness, flexible, mechanical and thermal properties. BMAs could produce UV-curable coatings of balanced coating performance with reasonably high biorenewable content. The results show that multi-arms acrylates based on bio-based polyols have great potential to replace petro-based photosensitive acrylates for surface coatings.

Acknowledgements

The researchers would like to thank the Fundamental Research Funds for the Central Universities (JUSRP111A08).

Reference

- [1] Marion N'Negue Mintsas, Laurence Lecamp, Claude Bunel, *Eur. Polym. J.* 45 (2009) 2043–2052.
- [2] Zhenglong Yang, Douglas A. Wicks, Junjie Yuan, Hongting Pu, Yongsheng Liu, *Polymer*. 51 (2010) 1572–1577.
- [3] Weiyi Xing, Ganxin Jie, Lei Song, Shuang Hu, Xiaoqi Lv, XinWang, Yuan Hu, *Thermochimica Acta*. 513 (2011) 75–82.
- [4] Johannes T.P. Derksen, F. Petrus Cuperus, Peter Kolster, *Prog. Org. Coat.* 27 (1996) 45-53.
- [5] Zhigang Chen, Bret J. Chisholm, Dean C. Webster, Ying Zhang, Sandeep Patel, *Prog. Org. Coat.* 65 (2009) 246–250.
- [6] Alessandro Gandini, *Macromolecules*. 41 (2008) 9491-9504.
- [7] Ying Xia, Richard C. Larock, *Green Chem.* 12 (2010) 1893-1909.
- [8] Michael A. R. Meier, Jurgen O. Metzger, Ulrich S. Schubert, *Chem. Soc. Rev.* 36 (2007) 1788–1802.
- [9] E. Dzunuzovic, S. Tasic, B. Bozic, D. Babic, B. Dunjic, *Prog. Org. Coat.* 52 (2005) 136–143.
- [10] Micah Black, James W. Rawlins, *Eur. Polym. J.* 45 (2009) 1433–1441.
- [11] Ong Hui Lin, R.N. Kumar, H.D. Rozman, Mohd. Azemi Mohd. Noor, *Carbohydrate Polymers*.

59 (2005) 57–69.

[12] Aruna Palanisamy, B.S. Rao, *Prog. Org. Coat.* 60 (2007) 161–169.

[13] Yong Hwan Kim, Eun Suk An, Seung Young Park, Bong Keun Song, *J. Mol. Catal B- Enzym.* 45 (2007) 39–44.

[14] Ying-Cen Guo, Giuseppe Mele, Francesca Martina, Eleonora Margapoti, *J Organomet. Chem.* 691 (2006) 5383–5390.

[15] H.P. Bhunia, G.B. Nando, T.K. Chaki, A. Basak, S. Lenk, P.L. Nayak, *Eur. Polym. J.* 35 (1999) 1381-1391.

[16] Archana Devi, Deepak Srivastava, *Mater. Sci. Eng A.* 458 (2007) 336–347.

[17] Archana Devi, Deepak Srivastava, *Eur. Polym. J.* 43 (2007) 2422–2432.

[18] Minakshi Sultania, J.S.P. Rai, Deepak Srivastava, *Eur. Polym. J.* 46 (2010) 2019–2032

[19] Zhigang Chen, Jennifer F.Wu, Shashi Fernando, Katie Jagodzinski, *Prog. Org. Coat.* 71 (2011) 98–109.

[20] Xiao Pan, Dean C. Webster, *Macromol. Rapid Commun.* 32 (2011) 1324–1330.

[21] Yongshang Lu and Richard C. Larock, *Biomacromolecules.* 9 (2008) 3332–3340.

[22] Leila Hojabri, Xiaohua Kong, Suresh S. Narine, *Biomacromolecules.* 11 (2010) 911–918.

[23] Chen Ning, Liu Ren, Liu Pengfei, Xun Chun, Zhang Shengwen, Liu Xiaoya, *International Congress on Imaging Science.* (2010) 654-658.

[24] A. Greco, D. Brunetti, G. Renna, G. Mele, A. Maffezzoli, *Polymer Degradation and Stability.* 95 (2010) 2169-2174.