

Advances in the Chemistry of Melamine Acrylate Oligomers

*Ahmet Nebioglu, Joseph A. Leon, Igor V. Khudyakov
Bomar Specialties, Torrington, CT, USA*

Abstract

Melamine resins are well known in the industry. We have prepared various very fast UV-curing melamine acrylates at low photoinitiator levels. A photoinitiator grafted melamine acrylate was also prepared showing low levels of leaching. We have obtained five oligomers through Michael addition of thiols to melamine acrylates. The most important property of the new sulfur containing oligomers is their high refractive index. These oligomers find applications in antireflective coatings.

Introduction

Melamine formaldehyde resins (MF) are used as crosslinkers to impart hardness, durability, chemical resistance, and heat resistance into automotive and industrial coatings.¹ MF resins are prepared by the reaction of melamine and formaldehyde under basic conditions followed by acidic etherification. All MF resins contain small amounts of unreacted formaldehyde (<0.1%). Much effort is devoted to reduce the formaldehyde content in MF resins.²

Melamine acrylates (MAs) can be dual cured with heat and UV light. Alkoxy groups of MAs react with hydroxyl groups at increased temperatures and acrylate unsaturations are UV-curable. MAs synthesized through the reaction of 2-hydroxyethyl acrylate (HEA) or acrylamide with melamine resins were reported before.^{3,4} We have earlier introduced a special grade of UV-curable melamine acrylate (**BMA-222**) with a unique chemistry to obtain a very low residual formaldehyde content. **BMA-222** can be easily UV-cured with 0.1 % photoinitiator.⁵

In this study, a photoinitiator grafted, self UV-curable (light-sensitive, LS[®]) version of **BMA-222** was synthesized. Furthermore, melamine acrylates with different number of acrylate functionalities were prepared. Reactions of the highly acrylated melamine with aromatic thiols led to high refractive index (n_D) MAs. Mechanical properties, cure response and refractive index of the melamine acrylates were investigated.

Experimental

Reagents

Thiophenol, triphenylmethanethiol, 2-mercaptothiazoline, 2-mercaptobenzo- thiazole, *p*-Thiocresol and 2-hydroxyethyl acrylate were purchased from Aldrich. Photoinitiators Omnirad 481 (1-hydroxycyclohexyl phenylketone) and Omnirad 73 (2-hydroxy-2-methyl-1-phenylpropanone) were products of IGM resins. Irgacure 2959 (1- [4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-

propane-1-one) was obtained from Ciba Specialty Chemicals. Melamine acrylate, **BMA-222** is a product of Bomar Specialties. The generic structures of mono-acrylate functional **XMA-220**, tri-acrylate functional **BMA-222**, penta-acrylate functional **XMA-224**, photoinitiator grafted **LS[®] XMA-222**, and sulfur containing high n_D **XMS-224** were shown in Figure 1.

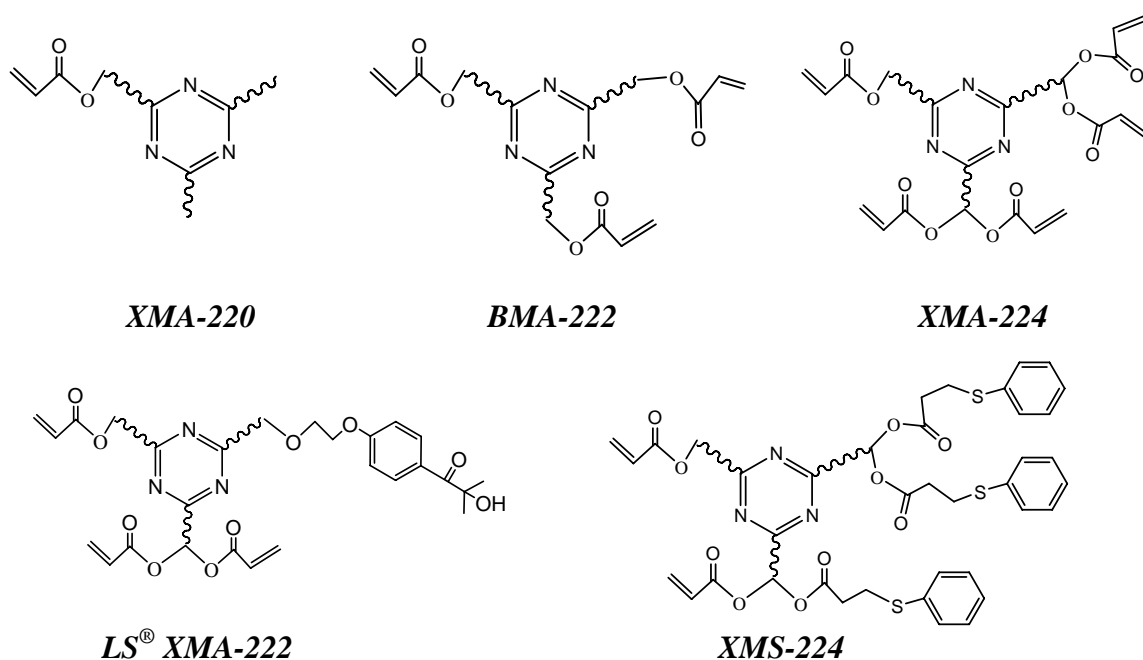


Figure 1. Generic structures of the chemicals used.

Instruments

All the products discussed in this study were analyzed with gel permeation chromatography (GPC) and infrared spectrometer (IR). GPC device of Polymer Labs PL-GPC 50 was equipped with an RI detector and mixed D-columns. The IR spectrometer was Perkin-Elmer Spectrum One model with a diamond crystal UATR. Formulations were cured in the air with a Fusion 300 processor, D-bulb, belt speed 20 ft/min, one pass. n_D of liquid oligomers were measured with Abbé refractometer. n_D of cured films were measured with a technique using different refractive index oils. In this method a sample of a cured film and a small amount of oil with a known n_D were squeezed in between glass microscope slides. When the refractive indices of the film and the oil were different, the boundaries of the film were visible through a Nikon transmission optical microscope. The Becke Line Method was utilized to narrow down the matching refractive index oil. The test was repeated until the refractive indices of the oil and the film matched. All measurements are done at the room temperature.

The viscosity was measured with a Brookfield RVT viscometer with a small adapter (spindle SC4-15 and cup 7R). The tensile properties of cured samples (elongation to break, tensile strength at break, tensile modulus) were measured with a Cheminstruments Tensile Tester-1000 system. The test method was designed to be in compliance with ASTM Standard D 882. The tester was controlled by the

Cheminstruments EZ-Lab system program. At least five samples of each cured formulation were studied at ambient temperature, to verify reproducibility of the data.

Results and Discussion

A special grade of UV-curing melamine acrylate (**BMA-222**) to obtain a good stability and low residual formaldehyde content was earlier introduced. It was reported that tri-acrylate functional **BMA-222** cures faster than the corresponding functionality urethane acrylates at a very low photoinitiator level (0.1%). In this study, two more melamine acrylate (MA) oligomers with different number of acrylate functionalities were produced. **XMA-220** and **XMA-224** have average acrylate functionalities of 1 and 5, respectively.

Tensile properties of the films formed upon UV-cure of formulations of MA oligomers were presented in Figure 2. Tensile strength of the penta-acrylate functional MA (**XMA-224**) had the highest tensile strength, probably due to an increased crosslink density. As expected, mono-acrylate functional MA (**XMA-220**) had the lowest tensile strength and highest elongation-at-break.

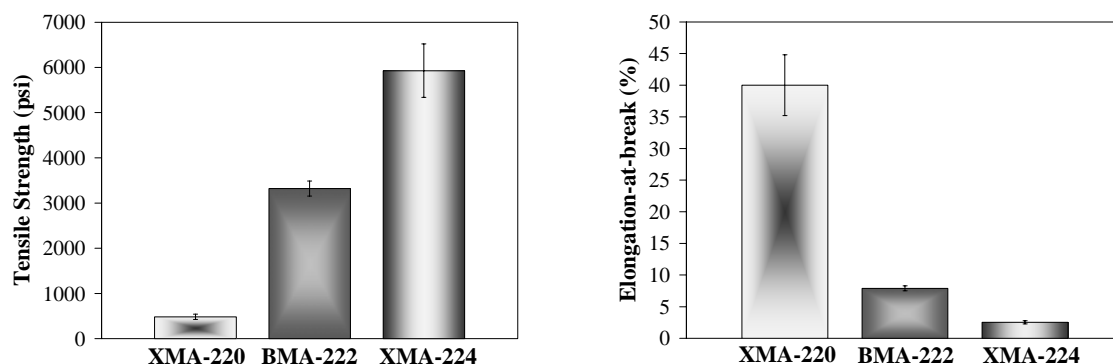


Figure 2. Tensile strength and elongation-at-break of MA-based formulations. Oligomers were formulated with 50% IBOA and 2% Omnirad 481.

Melamine acrylates are widely used in UV-curable wood coatings. Emission of volatile, extractable breakdown byproducts during UV-curing are often concerns for furniture, ink and food applications. There are extensive research on both academia and industry to develop non-migrating photoinitiators.^{6,7} MA oligomers can be a good choice to obtain low extractable containing films because of their fast cure response at low photoinitiator levels. **BMA-222** could be cured into tack-free films with even 0.1% Irgacure 2959 (a Food and Drug Administration approved photoinitiator). In order to further reduce the leaching of the photoinitiator, we have prepared tri-acrylate functional **LS[®] XMA-222** (an MA oligomer grafted with Irgacure 2959, cf. Figure 1). As a comparison, two formulations were prepared: one with **LS[®] XMA-222** (**F₁**) and the other with free Irgacure 2959 (**F₂**) (cf. Table 1). GC-MS analysis showed only residual amount of leached photoinitiator or its cleavage products to the solvent, THF. The amount of extractables from the films formed from **F₁** was 170 ppm, whereas it was 900 ppm for the films prepared from **F₂**. The concentration of grafted Irgacure 2959 in **F₁** was 2%. Considering that MA oligomers could be cured with very low photoinitiator concentration (0.1%), it is possible to get even much lower extractable content than 170 ppm with using **LS[®] XMA-222**.

Table 1. Formulations for the films prepared for GC-MS analysis

	F ₁ (wt. %)	F ₂ (wt. %)
LS [®] XMA-222	25	-
BMA-222	25	48
TPGDA	50	50
Irgacure 2959	-	2

MA oligomers can be used to increase mechanical properties of the urethane acrylate based UV-cured films. Formulations listed in Table 2 were prepared in order to observe the effect of the MA oligomers on tensile properties. BR-304⁸ is a flexible aromatic urethane acrylate. Formulations MA0, B10, B20, X10 and X20 contain 30 % IBOA and 2 % photoinitiator, Omnirad 481. L0 and L10 were prepared to elucidate the efficiency of LS[®] XMA-222 in UV-curing of urethane acrylate formulations.

Table 2. Urethane and melamine acrylate formulations

	MA0	B10 ^a	B20 ^a	X10 ^b	X20 ^b	L0 ^c	L10 ^c
BR-304	68 ^d	58	48	58	48	60	60
IBOA	30	30	30	30	30	30	30
Omnirad 481	2	2	2	2	2	-	-
BMA-222	-	10	20	-	-	9.2	-
XMA-224	-	-	-	10	20	-	-
Irgacure 2959	-	-	-	-	-	0.8	-
LS [®] XMA-222	-	-	-	-	-	-	10

^a“B” denotes BMA-222, numbers represent % concentration of BMA-222 in formulation

^b“X” denotes XMA-224, numbers represent % concentration of XMA-224 in formulation

^c“L” denotes LS[®] XMA-222, number(s) represent the % concentration of LS[®] XMA-222 in formulation

^dwt. % concentration

Tensile strength and elongation-at-break test values are presented in Figure 3. Tensile modulus comparisons were given in Figure 4. Films prepared from MA0 (do not contain any MA oligomer) had the lowest tensile strength and modulus, and highest elongation-at-break. Addition of just 10 % MA oligomers increased the tensile strength of the films by at least 6-fold. This increase could be attributed to the increased crosslink density. Further increase of MA concentration did not lead to an increase of tensile strength but increased the tensile modulus extensively. Penta-acrylate functional XMA-224 had the highest impact on modulus. Overall conversion of the acrylate groups were calculated by utilizing FT-IR. The decrease in the peak intensity of C-H stretching absorption band of the acrylates around 810 cm⁻¹ was used. Carbonyl C=O stretching band at 1720 cm⁻¹ was used as an internal standard. 10 % addition of either BMA-222 or XMA-224 increased the overall conversion. Further increase of BMA-222 or XMA-224 decreased the conversion of acrylates probably due to early vitrification during UV-polymerization.^{9,10} The film cured by using grafted Irgacure 2959, LS[®] XMA-222 (L10) demonstrated higher tensile strength and elongation-at-break compared to the film formed from a formulation containing BMA-222 and free Irgacure 2959 (L0). Modulus and overall conversion values of L0 and L10 were similar. This means that LS[®] XMA-222 worked very effectively for L10.

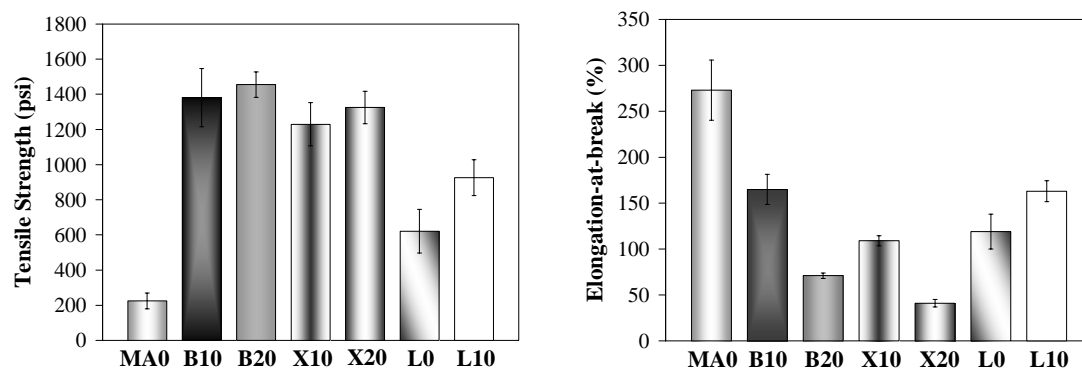


Figure 3. Tensile strength and elongation-at-break comparison of the films

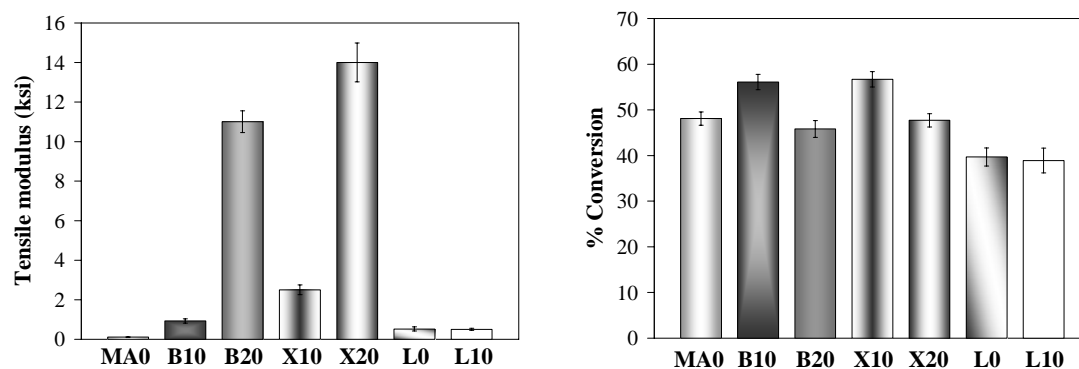


Figure 4. Tensile modulus and overall acrylate conversion of the films

High refractive index materials often obtained with inorganic/organic hybrid systems. However, to produce a transparent coating, metal oxide particles should be formed *in situ* at high temperatures ($>300^{\circ}\text{C}$). To the best of our knowledge, the highest reported refractive index organic polymer is n_D of 1.757.¹¹ At the same time, the polymer was not UV-cured but cast from a solvent.

There is commercial interest in coatings with high refractive index, which can be obtained at mild conditions, at ambient temperatures and with low or zero VOC. Therefore, UV-cured high n_D coating attract much attention from both academia and industry.¹² Besides all the known advantages of UV-curable formulations, UV-cure leads to increased n_D under cure due to an increase in molecular polarizability through molecular orientation and volume shrinkage.

Polymers containing aromatic groups and highly polarizable atoms such as nitrogen, sulfur, phosphorus, bromine, and iodine show relatively high refractive index values.^{13,14} Among these, sulfur containing polymers are of particular interest due to low color formation, raw material availability and variety of mechanical properties. MA oligomers have relatively high n_D of 1.512, due to relatively high concentration of (hetero)aromatic groups and nitrogen atoms. Michael addition reaction of thiols, RS-H to electron deficient enones such as maleimides¹⁵ and acrylates¹⁶ are well documented. Nucleophilic character of thiols, RS-H allows synthesis of C-S bond containing products with a high yield. In order to increase the refractive index (n_D) of MA oligomers, we have synthesized the thiols adducts of **XMA-224** through the reaction of aromatic thiols (cf. reagents section) with acrylate groups. As expected, the new thiol modified MA oligomers had higher refractive indices. In order to understand the effect of the

degree of thiol modification on refractive index value, **XMA-224** was modified with different amounts of thiophenol, i.e. thiol to initial acrylate ratio was changed. An increase of thiol to initial acrylate ratio resulted in an increase of n_D of the product as well. Addition of thiols to acrylates consumed the acrylate groups available for UV-cure, and hence decreased the tensile strength and toughness of the cured coatings. Therefore, there was a trade off between mechanical properties and refractive index.

Refractive indices of the melamine acrylates obtained via modification with various thiols were listed in Table 3. All the melamine acrylates gave transparent films after UV-cure. The cured oligomers had 1-5 % higher n_D compared to corresponding liquid oligomer. The structures of thiols essentially affect n_D of adducts, cf. Table 3. We were able to get n_D of modified melamine acrylate oligomers up to 1.6, cf. **XMS-2243** in Table 3. As expected, n_D of the oligomer and of the cured film were increased as the amount of aromatic groups in the thiol compound was increased (cf. **XMS-2241** vs. **XMS-2242** in Table 2). Further, alkyl groups usually lead to lower n_D of polymers due to a decrease in polarizability.⁴ In fact, **XMS-2244**, which has very similar structure to **XMS-224** except the presence of the methyl substituent in thiol, has lower n_D (cf. Table 2). **XMS-224** oligomer is particularly interesting for industrial application due to relatively low cost of raw materials, low color, and low viscosity (~5000 cP). Composition of three UV-curable formulations (denoted as **F**) based on **XMS-224** and physical properties of the cured films, **F_i** are presented in Table 4.

Table 3. High refractive index melamine acrylates

Oligomer	BMA	Thiol	n_D^a (oligomer)	$n_D^{a,b}$ (film)
XMA-224	–	–	1.512	1.521
XMS-224	BMA-224	Thiophenol	1.566	1.578
XMS-2241	BMA-224	2-Mercaptothiazoline	1.589	1.605
XMS-2242	BMA-224	2-Mercaptobenzothiazole	1.593	1.610
XMS-2243	BMA-224	Triphenylmethanethiol	1.600	1.620
XMS-2244	BMA-224	<i>p</i> -Thiocresol	1.555	1.565

^aDetermination error of n_D is ± 0.002 .

^bOligomers were UV-cured with 1% photoinitiator, Omnirad 73.

Table 4. Formulations and mechanical properties of **XMS-224** based films

	F₁	F₂	F₃	F₄
XMS-224 (wt.%)	99	69	49	-
XMA-224 (wt.%)	-	-	-	49
IBOA (wt.%)	-	30	-	-
TRPGDA (wt.%)	-	-	50	50
Omnirad 73 (wt.%)	1	1	1	1
Viscosity ^a (cP)	5400	400	150	100
Tensile Strength ^a (MPa)	87	270	399	6700
Elongation-at-break ^a (%)	8	30	5	3.3
Tensile Modulus ^a (MPa)	1.2	2.9	51	320
Durometer Hardness ^a	74	73	54	85

^aDetermination error is 10%.

Melamine acrylates (MA) with different number of acrylate functionalities were prepared. MA oligomers possess good curing response at very low photoinitiator levels (< 1%). Light-sensitive, photoinitiator grafted MA oligomer (**LS[®] XMA-222**) can be used as a photoinitiator and to improve mechanical properties. Novel UV-curable high n_D MA oligomers were also synthesized with utilizing the nucleophilic character of thiols. Among the oligomers synthesized, **XMS-224** is the most interesting because it has low viscosity, can be synthesized from readily available commercial raw materials, and its formulations produce colorless films after UV-curing. High n_D MA oligomers can be used in protective coatings for plastics and in antireflective coatings for wide variety of substrates.

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