

A Comparison of Maleimide Oligomers with Acrylate Oligomers

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Abstract

Maleimide oligomers and acrylate oligomers with identical backbones have been synthesized and characterized. Rheological studies show that the maleimide oligomers have higher viscosities than their acrylate analogs although their flow curves are both Newtonian. Coatings derived from maleimide oligomers are better in methylethylketone (MEK) resistance and stain resistance when compared acrylate oligomers. The effects of the end groups are decreased with an increase in the molecular weight of the oligomer.

Introduction

Success of the UV curing industry can be attributed to the high performance and variety of its raw materials, such as oligomers, monomers, photoinitiators, synergists, and other additives. In a UV curable formulation, oligomers provide the basic bulk properties of the final products. In order to meet different requirements in various applications, there are hundreds of oligomers for formulators to choose from. Among the oligomers commonly used in the UV curing industry cured by free radical mechanism, acrylates are the predominant choice. With more and more applications being explored, as well as higher and higher performance being required, there is a greater expectation on new and better oligomers.

Maleimide oligomers could be a potential substitute to acrylate oligomers in certain applications. The maleimide double bond is similar to the acrylate double bond in that they are both electron deficient and readily undergo free radical polymerization. Considering that the molecular weight range of commonly used oligomers is approximately 500-4000 g mol⁻¹, the maleimide functional group can comprise 5 to 50 weight % of the oligomer molecule. This can potentially differentiate maleimide oligomers from acrylate oligomers in mechanical properties and heat resistance, since they are widely used in the composites industry as matrix resins.

Maleimide compounds have been studied mainly as photoinitiators. The use of substituted maleimides to initiate polymerization by UV irradiation has been well studied by Hoyle and others.¹⁻⁴ It has been shown that maleimides efficiently initiate polymerization via an abstraction or electron transfer mechanism. However, the majority of these studies used the maleimide as a small molecule. Little is known about how maleimides behave when attached to an oligomer and the effect it has on rheology, photochemistry and the properties of cured polymers. In this study, we compare two maleimide end capped oligomers to acrylate oligomers of similar structure.

Experimental

All materials were used as received without further purification. Diisocyanate and polydiols were obtained from industrial sources. Hydroxyethylacrylate was obtained from Aldrich. N-Hydroxyethylmaleimide was prepared in our laboratories by standard methods. TMPEOTA, TMPTA and TRPGDA were obtained from UCB Chemicals Corporation. Benzophenone (BP), hydroquinonemonomethylether (MEHQ) and methylethylketone (MEK) were obtained from Aldrich. DC-57 and FC-4430 were obtained from Dow Corning and 3M, respectively. FirstCure HMPP (2-hydroxy-2-dimethyl-1-phenylpropane-1-one) was obtained from the Albemarle Corporation. Viscosities were measured using a Brookfield LV viscometer with small sample adapter at 25 °C, following mixing and allowing the formulations to set for 24 hours. Formulations were applied to Leneta charts (Form 5C) using a No. 3 wire round rod and cured under a Fusion UV Systems Aetek lamp at designed speed. Final cured films were then evaluated for these performance parameters:

- (1) Methylethylketone (MEK) double rubs were performed on cured films three minutes after exposure using a cheese cloth wrapped on a 8 oz. Ballpein hammer. Failure of the film was determined when there was a break in the continuous film.
- (2) Staining (mustard, red wine, and red shoe polish) was obtained after 24 hours and the tincture of KMnO_4 stain was determined after 5min; all stain materials were covered for the duration of the test period. Stain color density was measured using an X-Rite SpectroDensitometer, the uncoated white Leneta chart had a yellow color density of 0.13. Coatings were cured at 100 fpm with 26 mJ cm^{-2} of UVC.

Two prepolymers were prepared by reacting isophoronediiisocyanate with two polydiols to yield the polyurethane functional backbone with isocyanate end groups. The urethane prepolymer was further reacted with hydroxyethyl acrylate to yield the final oligomers, acrylate 1 (A1) and acrylate 2 (A2). The urethane prepolymer was also reacted with N-hydroxyethylmaleimide to yield two maleimide end capped urethane functional oligomers, maleimide 1 (MI1) and maleimide 2 (MI2). The molecular weight of A1 and MI1 are about 1500 higher than that of A2 and MI2 respectively. Rheological measurements were measured at 30°C with 25mm plate using a Rheometrics Dynamic Stress Rheometer.

Results and Discussion

Rheological Studies

Although high molecular weight (>20,000) polymeric materials are often non-Newtonian fluids, many UV curable oligomers belong to Newtonian category. As shown in Figure 1, the flow curves of the four oligomers we synthesized fit primarily Newtonian characteristics, their viscosities are relatively the same with the increase in shear rate. From Figure 1 we can also see that the viscosity difference between A1 and MI1 is much more significant then between A2 and MI2. This can be attributable to the difference in the end group. As a principle, with the increase of molecular weight, the effect of end group will become less and less important.

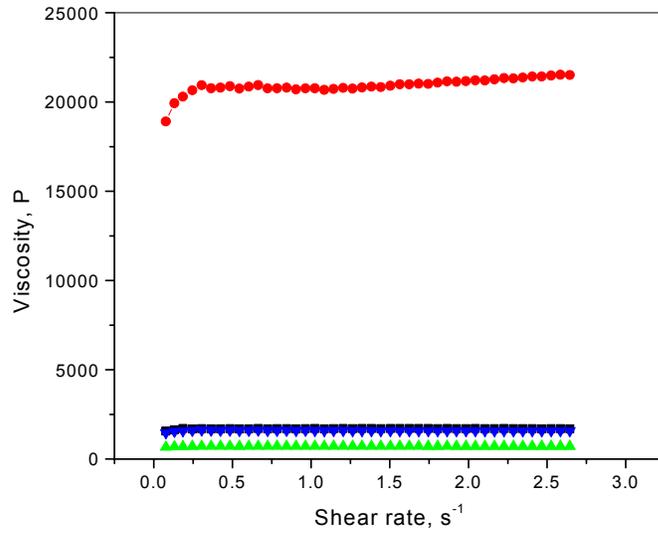


Figure 1. Flow curves of acrylate and maleimide oligomers (30°C):
(■) A1; (●) MI1; (▲) A2; (▼) MI2.

In Figure 2, the shear stress-shear rate curves show no thixotropic or rheopetic behavior for all four oligomers, which is a typical relationship for Newtonian fluids.

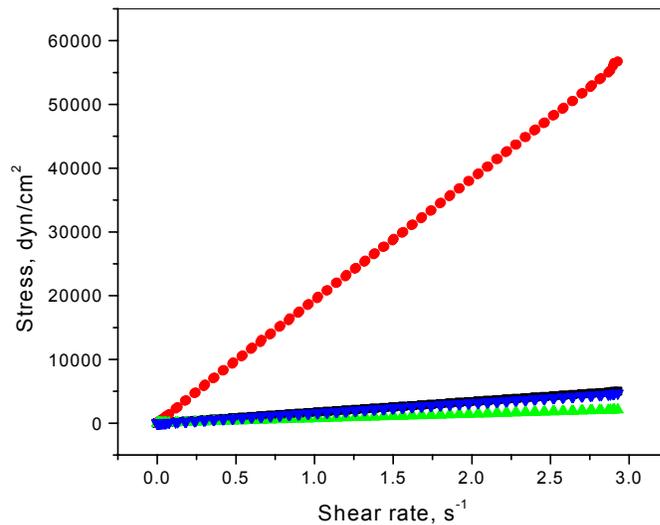


Figure 2. Shear stress—shear rate relationship of acrylate and maleimide oligomers (30°C):
(■) A1; (●) MI1; (▲) A2; (▼) MI2.

As presented in Figure 1, the maleimide derivatives were more viscous than the acrylate derivatives. The measured viscosity as a function of temperature for A1, A2, MI1, and MI2 are listed in Figure 3.

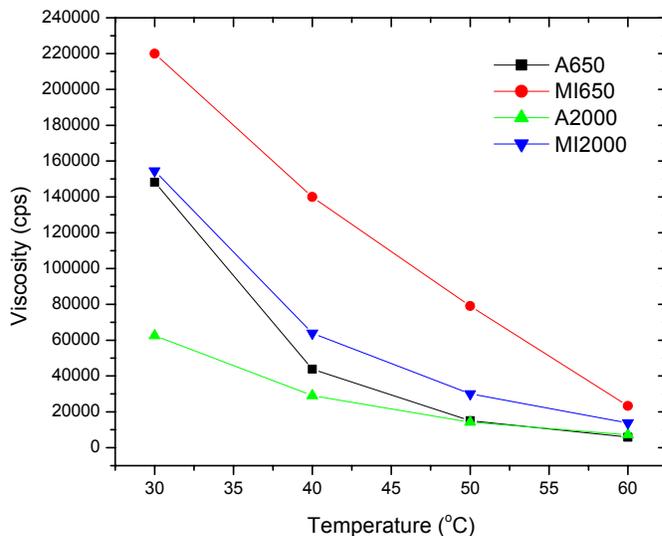


Figure 3. Viscosity as a function of temperature for acrylate and maleimide oligomers: (■) A1; (●) MI1; (▲) A2; (▼) MI2.

The acrylate oligomers showed an increase in viscosity with a decrease in molecular weight in the tested samples. The same observation was shown with maleimide oligomers. The effect may be attributed to the higher concentration of urethane functionality for the lower molecular weight oligomers, which could lead to an increase in hydrogen bonding. When comparing the acrylate oligomers to the maleimide oligomers, it is apparent that the maleimide end group has a greater effect on viscosity than the acrylate end group.

The effect of dilution on the viscosity of the acrylate and maleimide oligomers is shown in Figure 4. The acrylate oligomers, A1 and A2, show similar viscosities when diluted with TRPGDA. The maleimide oligomers, MI1 and MI2, also show similar viscosities upon dilution with TRPGDA beyond 40% dilution.

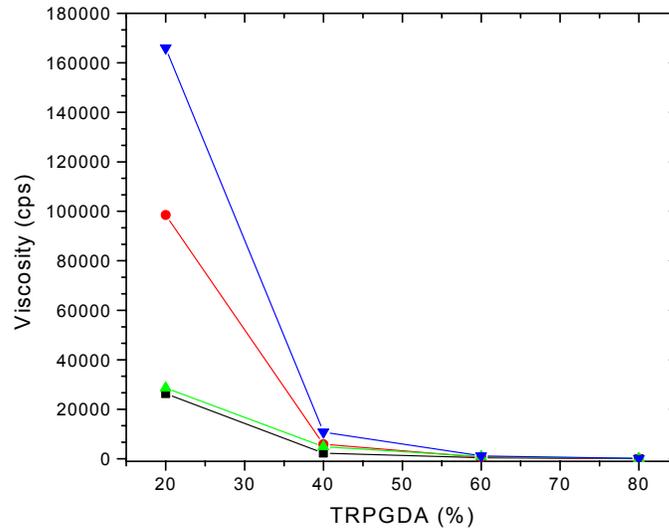


Figure 4. Viscosity as a function of % TRPGDA for acrylate and maleimide oligomers (25°C): (■) A1; (●) MI1; (▲) A2; (▼) MI2.

UV Curing study

An over print vanish (OPV) formulation was chosen as the test vehicle for evaluating the performance of the acrylate and maleimide oligomers. In the test formulations, the commonly used oligomer (acrylate epoxy) was replaced by A1, A2, MI1 and MI2. These formulations were cured then subjected to a battery of performance evaluations. The formulations and the corresponding viscosities are shown in Table 1.

Table 1. Formulations for A1, A2, MI1 and MI2.

Component	F1 (A1)	F2 (MI1)	F3 (A2)	F4 (MI2)
A1	30.0	---	---	---
MI1	---	30.0	---	---
A2	---	---	30.0	---
MI2	---	---	---	30.0
*Monomer mix	58.98	58.98	58.98	58.98
BP	5.0	5.0	5.0	5.0
HMPP	0.8	0.8	0.8	0.8
AS4	3.0	3.0	3.0	3.0
FC4430/DC57	0.1/2.0	0.1/2.0	0.1/2.0	0.1/2.0
MEHQ	0.02	0.02	0.02	0.02

Viscosity (cps at 25 °C)	353	589	721	917
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*Monomer mix = TRPGDA/TMPTA/TMPEOTA (20/25/55)

Performance results for the acrylate and maleimide oligomers are shown in Table 2. Solvent resistance (MEK double rubs) showed that the coatings from maleimide oligomers performed better in resistance to MEK than those from acrylate oligomers. Staining results for KMnO₄, mustard, red wine and shoe polish, show that all performed similarly.

Table 2. Results for the performance evaluations.

Performance Parameter	F1 (A1)	F2 (MI1)	F3 (A1)	F4 (MI1)
Solvent resistance (MEK double rubs)	21	36	8	18
KMnO ₄	0.26	0.24	0.39	0.37
Mustard	0.40	0.41	0.63	0.64
Red wine	0.14	0.14	0.15	0.15
Shoe polish	0.26	0.24	0.39	0.37

Conclusions

Maleimide and acrylate end capped oligomers were synthesized and compared for rheology and curing performance. The maleimide end group shows a significant effect on the viscosity when compared to the acrylate end group. When used in place of an oligomer, the maleimide oligomers showed equal and/or superior performance to the acrylate oligomers.

References

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