Novel Ultra Low Viscosity Epoxy for Enhancing the Tg and Processability of Multifunctional Thermosets

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ABSTRACT

Multifunctional epoxy resins such as novolacs offer high glass transition temperatures (Tg), and an excellent combination of physical and mechanical properties following cure. Due to their high viscosity, novolacs are used in conjunction with a solvent or diluent, which also drastically reduces Tg while acting as processing aids to reduce viscosity. In this work, we introduce a novel ultra-low viscosity epoxy molecule, XU 19127, based on divinylbenzene dioxide. This new epoxy offers unprecedented viscosity-cutting power for orders-of-magnitude viscosity reduction, while actually enabling an increase in Tg through enhanced molecular rigidity. The potential to harness this unique molecule for high Tg formulations will be demonstrated. The effect of this novel molecule on the rheology, cure behavior, and thermo-mechanical properties of formulations intended for high Tg applications will be explored.

1. INTRODUCTION

Epoxy novolacs (EPNs) are multifunctional epoxies based on phenolic formaldehyde novolacs. (Figure 1) The viscosity of EPNs resins range from a high-viscosity liquid of n=0.2 to a solid of n> 4. (Table 1) The multifunctionality of these resins provides high cross-linking density, leading to improved thermal and chemical resistance properties when compared to di-functional bisphenol A epoxy resins. Curing agents such as aromatic amines and anhydrides, can be used to achieve thermosets with high Tg. The improved thermal properties and chemical resistance of EPNs-based thermosets are very useful in many demanding applications ranging from aerospace to oil and gas. [1-3]

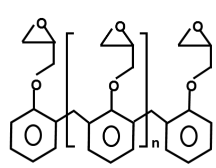


Figure 1. Structure of multifunctional novolac epoxy resin

Due to the high viscosities of EPNs, they are frequently used in conjunction with a solvent or diluent. The typical epoxy reactive diluents are derived from reactively compact hydroxyl containing compounds, such as alcohols, glycols, phenols, and epichlorohydrin. Some common commercial glycidyl ether reactive diluents are n-butyl glycidyl ether (BGE), C12-C14 aliphatic glycidyl ether, o-cresol glycidyl ether, neopentylglycol diglycidyl ether, and butanediol diglycidyl ether (BDDGE). [1,2] Typically, these epoxy reactive diluents have very low viscosity (1-70 mPa·s) at 20°C relative to standard liquid epoxy resin (11,000-16,000 mPa·s). The chloride content is up to 5% due to the nature of the manufacturing process. However, the use of these reactive diluents often results in decreased chemical resistance along with reduced thermal and mechanical properties for the cured thermoset.

Table 1. Typical properties of epoxy phenol novolacs

Property	**D.E.N.™ 431[a]**	**D.E.N. 438[a]**	**D.E.N. 439[a]**
n	0.2	1.6	1.8
EEW[b]	175	178	200
Viscosity, mPa·s	1400[c]	35,000[c]	3,000[d]
Softening point, °C			53
Color, Gardner	1	2	3

a. Olin Epoxy
b. Epoxide equivalent weight
c. Temperature of measurement=52°C
d. Temperature of measurement=100°C [1]

In this work, we introduce a novel ultra-low viscosity epoxy molecule, XU 19127, based on divinylbenzene dioxide, which consists of two epoxide groups directly bound to aromatic ring, as shown in Figure 2. [4] The unique structure of XU 19127 enables a synergy of attractive physical and chemical properties, such as low viscosity, high glass transition temperature, and rapid UV cure. [5] Produced by an epoxidation process that does not involve epichlorohydrin, XU 19127 contains zero chloride which is attractive for many electronic applications.[4] In addition, XU 19127 is compatible for use with typical amine or anhydride curing agents, which ensures a broad range of potential composite processing applications.

Improving the processability of multifunctional epoxy resins such as novolacs with no compromise to the thermal stability is of significant interest, particularly in demanding applications that require composite structures with Tg > 200 ºC. Although such structures tend to be fabricated using a variety of methods ranging from Prepregs to filament winding, extremely high viscosity would pose a processing constraint irrespective of the fabrication method used. The goal of this work is to explore the potential to alleviate the processing constraints associated with EPNs while delivering Tg > 200 °C, using XU 19127 as an additive. The effect of this novel molecule on the rheology, cure behavior, and thermo-mechanical properties of formulations intended for high Tg applications will be explored.

2. EXPERIMENTATION

2.1 Materials

Epoxy Resins

XU 19127 is a commercially available divinylbenzene dioxide (DVBDO) from Olin Epoxy. D.E.N.™ 438 Epoxy Novolac Resin (Olin) is a semi-solid reaction product of epichlorohydrin and phenol-formaldehyde novolac with multi-epoxy functionality (3.6). 1,4-Butanediol diglycidyl ether (BDDGE) is a bifunctional reactive diluent of aliphatic glycidyl ether used to reduce the viscosity of epoxy resin. BDDGE is commercially available from Olin Epoxy as D.E.R.™ 731. D.E.R.™ 383 is a bisphenol A based liquid epoxy resin.

Curing Agents

Lindride 25k is a blend of methyl-5-norbornene-2,3-dicarboxylic anhydride, 5-norbornene-2,3-dicarboxylic anhydride, 1-(2-hydroxypropyl) imidazole, which is commercially available from Lindau Chemicals, Inc.[6] Diethyltoluenediamine (or DETDA) is an aromatic amine curing agent, which is obtained from Albemarle Corporation. Isophorone diamine (or IPDA) is a cycloaliphatic amine curing agent, which is obtained from Evonik Industries AG. Jeffamine® D230 is a polyetheramine curing agent, which is obtained from Huntsman Corporation. Diethyenetriamine (DETA or D.E.H.™ 20) is aliphatic amine curing agent available from Olin Epoxy.

2.2 Procedures

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analysis is performed using a Q2000 model DSC from TA Instruments, which was equipped with an auto sampler and a refrigerated chiller system (RSC). Approximately 10 grams (g) of a formulated sample was mixed by using a FlackTek mixer (at 2,000 revolutions per minute [rpm] for 2 minutes). Then, 5-10 milligrams (mg) of the resulting sample was transferred to a hermetic aluminum pan (Hermetic aluminum pan is purchased from TA Instruments with part number: TA 900793-901/900794-901). The pan was sealed and placed in the auto-sample tray. A brief description of the method of the DSC analysis is as follows:

Table 2. Method of DSC analysis

Stage	Conditions
1	Equilibrate at 25°C
2	Ramp 10°C/min to 250°C
3	Mark end of cycle 1
4	Equilibrate at 30°C
5	Mark end of cycle 2
6	Ramp 10°C/min to 250°C
7	End of method

Thermal Rheology Analysis

The thermal rheology analysis was performed in Discovery Hybrid Rheometers (DHR) from TA Instruments with 40mm, 2 deg plate (Serial number 106204).

Thermogravimetric Analysis (TGA)

Weight loss was measured using a Q500 thermogravimetric analysis (TGA) instrument (TA instruments). A standard DSC pan was zeroed on the TGA, filled with about 10 mg of sample, then loaded back into the instrument for analysis. The sample was heated under nitrogen from room temperature to 300°C at 5°C/min.

3. RESULTS

3.1 Comparison of standard liquid epoxy resin, BDDGE, and Olin's ultra-low viscosity epoxy resin (XU 19127)

Table 3 shows the comparison of standard liquid epoxy resin, BDDGE, and Olin's ultra-low viscosity epoxy resin (XU 19127). BDDGE is a commonly used commercial glycidyl ether reactive diluent. Epoxide equivalent weight (EEW) of standard liquid epoxy resin is around 180 g/eq, EEW of BDDGE is 130-145 g/eq, while EEW of XU 19127 is about 78-86 g/eq. The viscosity of BDDGE or XU 19127 at 25°C is ca. 20 mPa·s, which is about 600 times lower than standard liquid epoxy resin.

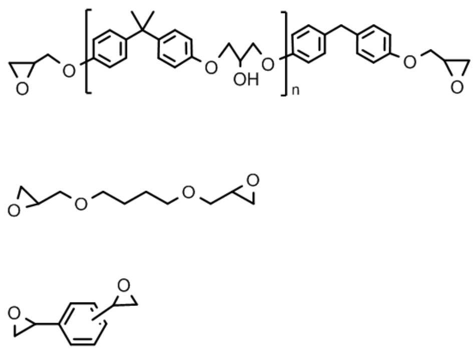
Unlike standard liquid epoxy resin and BDDGE, XU 19127 does not have hydrolyzable chloride, since the manufacturing process does not involved epichlorohydrin. However, the difference between XU 19127 and a reactive diluent such as BDDGE is clearly evident upon comparing the Tg following cure. When cured with IPDA, XU 19127 has a Tg of 223 °C, which is 200 °C greater than the corresponding Tg for BDDGE and 44 °C higher than the Tg of a di-functional bisphenol A epoxy resin. The Tg of XU 19127 is compared with bisphenol A epoxy resin for various curing agents such as aliphatic amine (DETA), cycloaliphatic amine (IPDA), or aromatic amine (DDS), in Table 3. The Tg of thermoset cured with XU 19127 is 14-44°C higher than the Tg of thermoset cured with standard liquid epoxy resin, depending on the curing agent used.

Table 3. Comparison of standard liquid epoxy resin, BDDGE, and ultra-low viscosity epoxy resin (XU 19127)

	Standard Liquid Epoxy Resin	**BDDGE**	**Ultra-Low Viscosity Epoxy Resin (XU 19127)**
EEW (g/eq)	180	130-145	78-86
Viscosity, mPa·s (25 °C)	12,000	24	20
Hydrolyzable Chloride (ppm)	500	2,000	ND[a]
Tg with Various Curing Agent (°C)			

Aliphatic Amine (DETA)	90	NA[b]	110
Cycloaliphatic Amine (IPDA)	179	23	223
Aromatic Amine (DDS)	224	NA	238

a. ND: Hydrolyzable chloride is not detected.
b. NA: Data is not available.



DGEBA liquid epoxy resin

BDDGE

DVBDO (XU 19127)

Figure 2. Chemical structures of DGEBA liquid epoxy resin, BDDGE, and DVBDO (XU 19127)

The chemical structures of DGEBA liquid epoxy resin, BDDGE, and XU 19127 are shown in Figure 2. While diluents such as BDDGE are composed of aliphatic groups, which result in a flexible structure, the direct attachment of epoxy groups to the aromatic ring in the case of XU 19127 results in an extremely rigid structure. The rigid structure and high content of aromatic rings of XU 19127 significantly boost the thermal properties of the cured thermoset.

3.2 High Tg formulations using XU 19127

Blends of multifunctional novolacs epoxy resin and XU 19127 were prepared in the lab to evaluate rheology, cure behavior, and thermo-mechanical properties of formulations intended for high Tg applications. D.E.R. 383 represents a standard di-functional bisphenol A based liquid epoxy resin and D.E.N. 438 is multifunctional novolac epoxy resin with average functionality of 3.6. Due to the low viscosity of XU 19127, it is very amenable to blending as an additive with liquid epoxy resin or novolac epoxy resin to create various resin formulations, for example, Blend 1 and 2 listed in Table 4.

Table 4. Viscosity and Tgs of multifunctional novolac epoxy blends

	XU 19127	**D.E.R. 383**	**D.E.N. 438**	**Viscosity@50°C (Pa·s)**
Blend 1	15	85		0.23
Blend 2	15		85	4.35
XU 19127				0.020 at 25°C
D.E.R. 383				0.69
D.E.N. 438				31

Rheology of blends

The thermal rheology analysis was performed in Discovery Hybrid Rheometers (DHR). The viscosity of various resins from 20 to 80 °C is shown in Figure 3. At 40 ºC, the incorporation of only 15% XU 19127 results in more than 20x reduction of viscosity. As a comparison, the reduction observed with a diluent such as BDDGE is also shown in Figure 3. The viscosity of pure D.E.N. 438 is about 31 Pa·s at 50°C, while the viscosity of a blend of 85% D.E.N. 438 and 15% XU 19127 is only 4.35 Pa·s at 50°C, which is comparable to the viscosity reduction achieved with a diluent such as BDDGE.

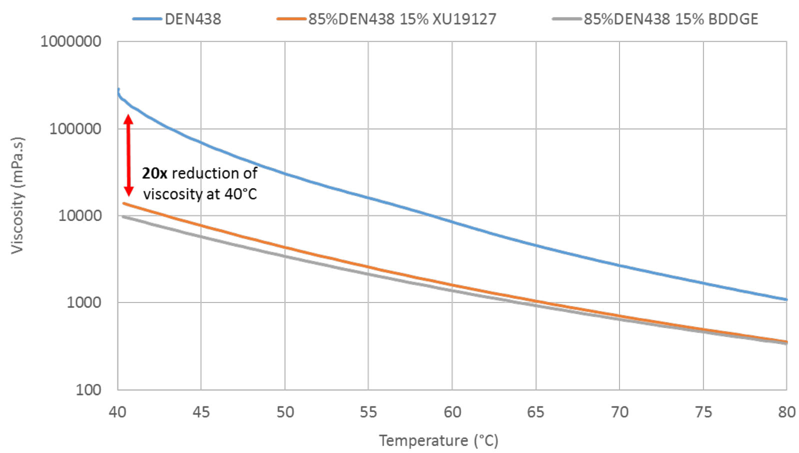


Figure 3. Viscosity vs. Temperature of XU 19127 and D.E.N 438 blended mixture

Curing behavior of blends

The curing behavior of blend is analyzed by DSC analysis (Figure 4). The resins of D.E.N. 438 or blend of 85% D.E.N. 438 and 15% XU 19127 are mixed with curing agent Lindride 25k and the heat flow vs. temperature is collected in DSC in order to monitor the reaction progress. The exotherm onset temperature and peak temperature for the cure reaction of D.E.N. 438 remains unchanged upon addition of 15 % of XU 19127, which shows no change in the cure kinetics as a consequence of the addition. A slight increase in the overall magnitude of the exotherm or the heat of reaction is observed due to the lower EEW of XU 19127 resin. Based on this example, incorporation of XU 19127 does not affect the curing behavior of the base epoxy resin. However, the lower molecular weight of XU 19127 can make the monomer more sensitive to temperature-induced volatilization, as shown in Figure 5. This issue can be overcome by building up the molecular weight of the formulation through curing at a lower temperature or using a catalyst before subjecting the formulations containing XU 19127 to temperatures over 100 ºC. Once fully cured, formulations containing XU 19127 exhibit outstanding Tg and thermal stability.

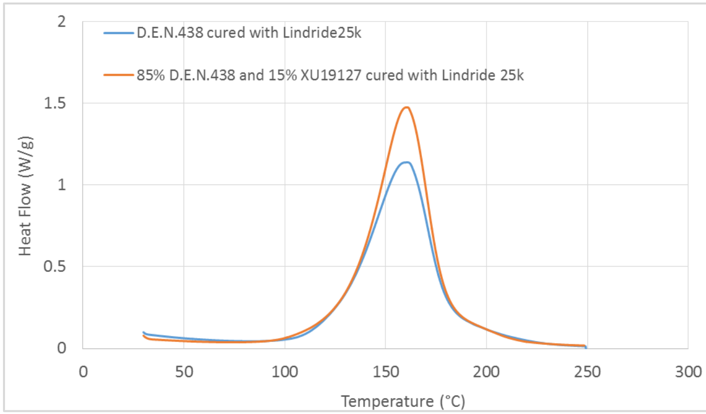


Figure 4. DSC analysis of D.E.N. 438 or blend of 85% D.E.N. 438 and 15% XU 19127 cured with Lindride 25k

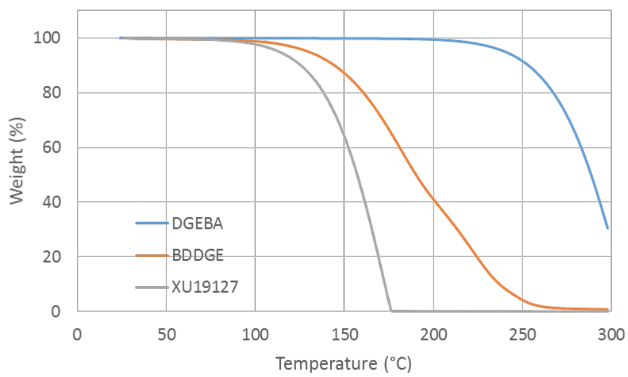


Figure 5. TGA of DGEBA, BDDGE and XU 19127 epoxy resin

Glass transition temperature (Tg) with various curing agents

Aromatic amines, like DETDA and anhydrides based on nadic methyl anhydride (NMA), usually provide high glass transition temperature (Tg) when cured with epoxy resin. To measure the Tg of the thermoset, the epoxy resin and curing agent are mixed and then cured in an oven with a curing cycle of 12 hours at 90°C, 1 hour at 150°C, 1 hour at 200°C, and 1 hour at 230°C. After curing is completed, Tg is measured through DSC.

As shown in Figure 6, when cured with Lindride 25k, the Tg of D.E.N. 438 is 205°C, the Tg of 85% D.E.N. 438 and 15% XU 19127 is 213°C, while the Tg of 85% D.E.N. 438 and 15% BDDGE is only 185°C. Unlike the common commercial glycidyl ether reactive diluents like BDDGE, this novel ultra-low viscosity epoxy resin (XU19127) can further increase the glass transition temperature (Tg) of multifunctional novolac epoxy resin. The similar effects are observed when aromatic amine (DETDA) is used as curing agent. In fact, with either curing agent, the Tg obtained when adding only 15% of XU 19127 is even higher than the Tg of the multifunctional novolac resin. This is particularly impressive, when considering that the Tg increase by blending XU 19127 with a multifunctional novolac resin is accompanied by a 20X reduction in viscosity when compared to the viscosity of the base multifunctional resin. To the best of the authors' knowledge, there have been no other demonstrated additives or methods that could actually achieve a similar viscosity reduction while accompanied by an increase in Tg. The effect of XU 19127 on the overall increase in Tg of the multifunctional novolac blend could be explained by an increase in concentration of rigid aromatic groups and a consequently restricted segmental mobility of the polymer network. The potential to utilize this novel molecule for UV cure will be presented in future work.

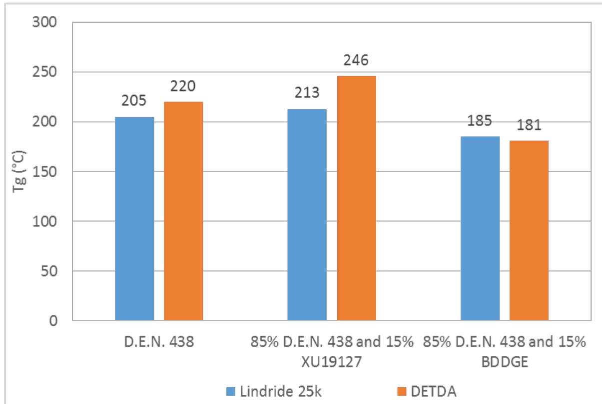


Figure 6. Tg of D.E.N. 438, 85% D.E.N. 438 and 15% XU19127, 85% D.E.N. 438 and 15% BDDGE cured with Lindride 25k or DETDA

4. CONCLUSION

In summary, the novel ultra-low viscosity epoxy molecule (XU 19127) provides an unprecedented balance of viscosity-cutting power for orders-of-magnitude viscosity reduction, as well as an increase in Tg through enhanced molecular rigidity. In addition, XU 19127 also exhibits other benefits like zero chloride content and rapid UV cure, which are well-suited for electronics or 3D printing applications. In this work, we demonstrated the potential to achieve Tg > 200 ºC with either an aromatic amine or anhydride curing agent, while facilitating a drastic enhancement in processability of a multifunctional novolac resin through significant viscosity reduction. While reactive diluents such as BDDGE also enable viscosity reduction, they decreased the Tg of the novolacs far below 200 ºC. The viscosity reduction and increase in Tg was achieved with no change in the cure kinetics of the resin. The unprecedented balance of Tg enhancement and viscosity reduction are enabled by the unique molecular structure of XU 19127.

5. REFERENCES

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