BIO-BASED THERMOSETS PREPARED USING MICHAEL ADDITION OF FURAN AND ISOSORBIDE BUILDING BLOCKS

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ABSTRACT

The Michael addition reaction of (meth)acrylates with amines can be used for the preparation of thermosets for coating applications because its fast reaction kinetics allow for rapid curing at low temperatures. Furan-based building blocks have been investigated as alternatives to incumbent phenolic systems and were found to possess good mechanical and barrier properties. Multifunctional furan-based amine cross-linkers and isosorbide methacrylate (IM) were used to create thermosets utilizing the Michael addition reaction. The system can be cured at low temperatures in a relatively short period of time while yielding good thermal and mechanical properties due to high functionality of the amine cross-linkers and the high reactivity of IM. In this investigation, the new systems' cure behavior of these new systems was investigated using spectroscopic techniques. The relative reactivity of primary and secondary amines was evaluated and formulations with IM conversion greater than 90% were obtained.

1. INTRODUCTION

This work investigates combining furanyl and isosorbide building blocks into one polymer network system by reacting isosorbide methacrylate with furan-based di-amine DFDA utilizing Aza-Michael addition reaction. Typical 'Michael donors' include enolates, amines, thiols, and phosphines; typical 'Michael acceptors' include methacrylates, acrylates, acrylamides, maleimides, acrylonitriles, cyanoacrylates, and vinyl sulfones [4]. This study prioritizes Aza-Michael addition reaction of methacrylates with amines, which can be used to prepare thermosets for coating, composite, and additive manufacturing applications where fast reaction kinetics are needed for rapid curing at low temperatures. The reaction proceeds with no by-products. Bio-based resins were used for study in which the reactivity of primary and secondary amine moieties with methacrylate functional monomers was investigated. The resulting information was used to design a formulation that results in a polymer system that possess high glass transition temperature and high glassy state storage modulus. There is a great diversity of plant biomass that can serve as feedstocks for the generation of alternative monomers and novel thermosetting polymers designed for performance characteristics associated with coatings, composites and adhesives. Isosorbide methacrylate is one of the potential candidates for high

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performance bio-based thermosets. Its low viscosity is advantageous in liquid molding and additive manufacturing processes. IM forms a crosslinked polymer network via homo-polymerization. The resulting ploymer possesses a high glass transition temperature (215°C) with good UV resistance [3]. DFDA is another biobased monomer of interest that has been found to impart good thermomechanical characteristics when used as curing agent in epoxy formulations [2]. Hu et al. successfully synthesized a fully furan-based thermosetting polymer with a glass transition temperature of 56°C and storage modulus of 3.5 GPa at room temperature [2]. By hybridizing bio-based chemical structures using different building blocks, J. R. Mauck et al. obtained epoxy thermosets using lignin-derived epoxy and DFDA amine hardener with a substantially excellent thermomechanical and thermogravimetric properties [5]. One goal of this work is to combine the isosorbide and furan building blocks using Michael addition of IM and DFDA to tune mechanical properties of the resulting thermoset polymer. It is known that the reactivity of secondary amines generated from the Michael addition reaction of methacrylates with primary amines can be significantly lower than the primary amine reaction. Therefore, the relative reaction of primary and secondary amines was investigated in an effort to help guide the design of networks based on IM and DFDA.

2. EXPERIMENTATION

2.1 Synthesis of Furan-Based Diamine (DFDA)

A coupling reaction of furfuryl-amine (99%, Sigma-Aldrich) using formaldehyde solution (37%, Sigma-Aldrich) was used to synthesize a furan-based di-amine (DFDA) as shown in **Figure 1.** All materials were used as received. The DFDA was purified by distillation after extraction in chloroform to reach a purity of 99%, as characterized by ^{1}NMR.

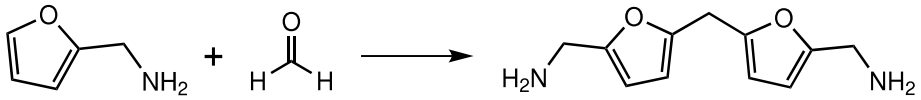


Figure 1. Reaction scheme for the preparation of furan-based di-amine (DFDA).

2.2 Synthesis of Isosorbide Methacrylate (IM)

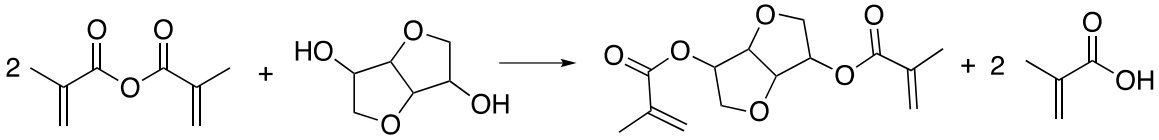


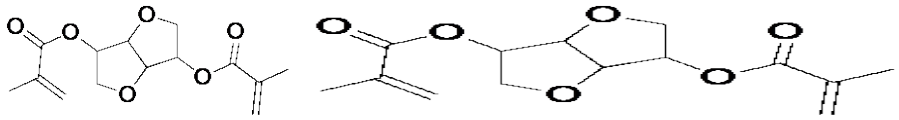
Figure 2. Reaction scheme for the preparation of isosorbide methacrylate (IM).

Isosorbide methacrylate was synthesized using isosorbide (98%, Sigma-Aldrich), methacrylic anhydride (99%, Sigma-Aldrich), and the catalyst 4-dimethylamino pyridine (DMAP 99%, Sigma-Aldrich) [3]. The reaction is shown in **Figure 2**. Hydroquinone (ACS Reagent Plus ≥ 99%, Sigma Aldrich) was used as a free radical inhibitor to prevent free radical homo-polymerization.

All materials were used as received without further purification. The IM used had a purity of 98%, characterized by ^{1}H NMR and FTIR after purification.

2.3 Reactivity Studies of Methacrylate with Primary and Secondary Amine Moieties

IM, DFDA and the commercially available diamine Jefflink 754 (Huntsman) shown in **Figure 3** were used for the reactivity studies. These studies were conducted using a Nicolet IS50 FTIR spectrometer in transmission mode and in the near infrared (NIR) frequenct range. Reaction studies were conducted at 60° on one to one molar mixtures of IM with DFDA, and IM with Jefflink 754. DFDA contains primary amines that upon reaction with IM form secondary amine moieties. Jefflink 754 diamine, on the other hand, only contains secondary amine groups that are structurally similar to the secondary amine on DFDA formed from Michael addition with IM. The peak locations for primary amine and methacrylate (located at 4940 cm^{-1}, 6160 cm^{-1}) were used to determine the conversion of the respective functional groups. The secondary amine peak (located at 6160 cm^{-1}) was monitored for secondary amine conversion.



a. b. c.

Figure 3. Chemical structures of isosorbide methacrylate (a), DFDA(b) and JEFFLINK 754(c).

2.4 Sample Preparation

DFDA, IM and DGEBA (Miller) were used to formulate a network system. DFDA and IM were blended in a molar ratio of 2:1 to ensure the low viscosity of resulting resin blend after curing by Michael addition. The result was as liquid with a glass transition of -35 °C, characterized by DSC. This was then blended with DGEBA using a THINKY centrifugal mixer at a speed of 1600 rpm for 3 minutes, then de-gassed for one minute, and then poured into a silicone mold. The composition by mass fraction of this polymer system was 23% DFDA, 15% IM, and 62% DGEBA. The samples were cured using the following procedure: 60 °C for 3 hours, and post-cure at 160 °C for 10 hours. Near-infrared spectroscopy was used to characterize the cured materials. Within the limits of the technique, the analysis showed that full cure of methacrylate, epoxy, and amine was achieved.

2.5 DMA

Dynamic Mechanical Analysis was performed on polymer samples prepared as discussed in Section 2.4, using a TA Instruments Model Q 800 instrument to evaluate the glass transition temperature (T_g) and storage modulus of the polymer. DMA tests were conducted using single cantilever geometry at a frequency of 1 Hz and amplitude of 10 μm. Sample dimensions were

3mm×12.5mm×17.5mm. The temperature was increased at ramp rate of 2 °C/min from –100 °C to 180 °C. T_g was obtained from both the loss modulus and tan$\boldsymbol{\delta}$ peak positions.

3. RESULTS

3.1 Reactivity of Methacrylate with Primary and Secondary Amine Moieties

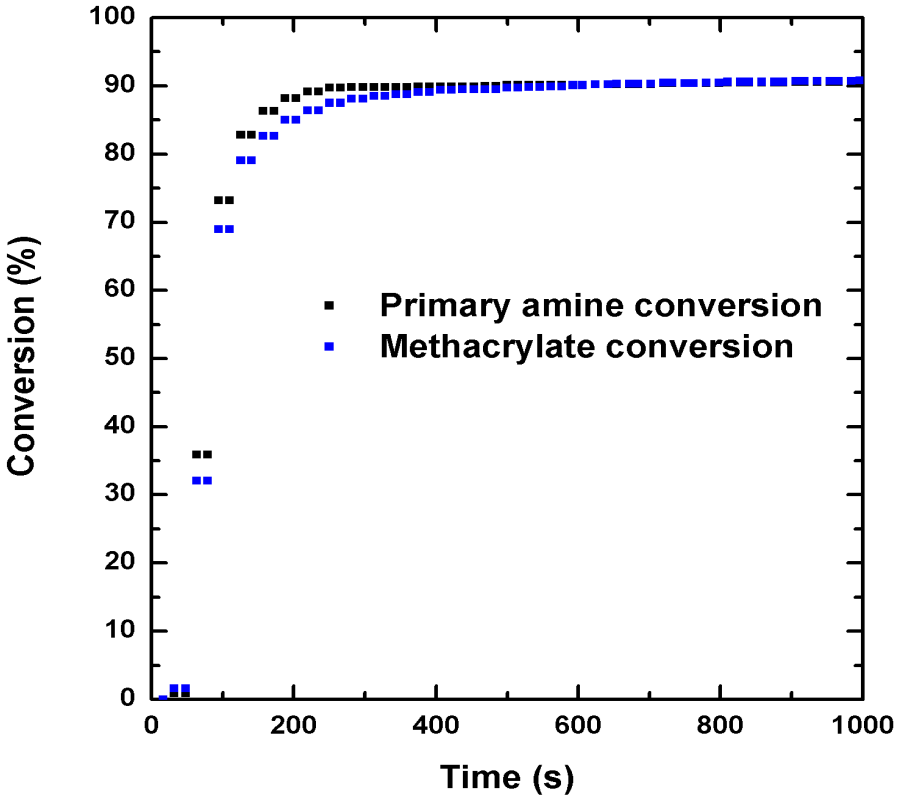


Figure 4. Conversion vs. time of primary amine and secondary amine of DFDA/IM system.

Figure 4. shows conversion with respect to time of primary amine groups and methacrylate groups when reacting DFDA with IM on one to one molar ratio. The conversions, for methacrylate and primary amine groups both go up to 94% within the first 10 mins. At the end of this study, the resin system did not crosslink. The result was a liquid with a glass transition of -35 °C, characterized by DSC. This study suggests the reactivity limitation between methacrylate groups and secondary amine moieties that are formed upon reaction with IM. The reactivity of secondary amine groups with methacrylate groups in this system is difficult to measure using N-IR characterization due to the overlapping peaks of the primary and secondary amine groups. To isolate secondary amine group reactivity from primary amine groups reactivity, Jefflink 754 diamine, which only contains secondary amine groups that are structurally similar to the secondary amine on DFDA formed from Michael addition with IM, was used to react with IM. **Figure 5** shows the reaction profile for this experiment monitored using N-IR in blue. The final secondary amine groups conversion was found to be 8% which clearly shows the limitations of

reactivity of this type of secondary amine relative to the primary amine found in IM. **Figure 5** compares methacrylate groups conversion for the IM/DFDA system and IM/Jefflink 754 system which further illustrates the large disparity in reaction rates.

Therefore, to formulate crosslinked systems using IM and DFDA, a secondary cross-linker is necessary. DGEBA was used for this purpose was blended into the resin system to achieve a full conversion of primary and secondary amine groups on DFDA as described in the experimental section.

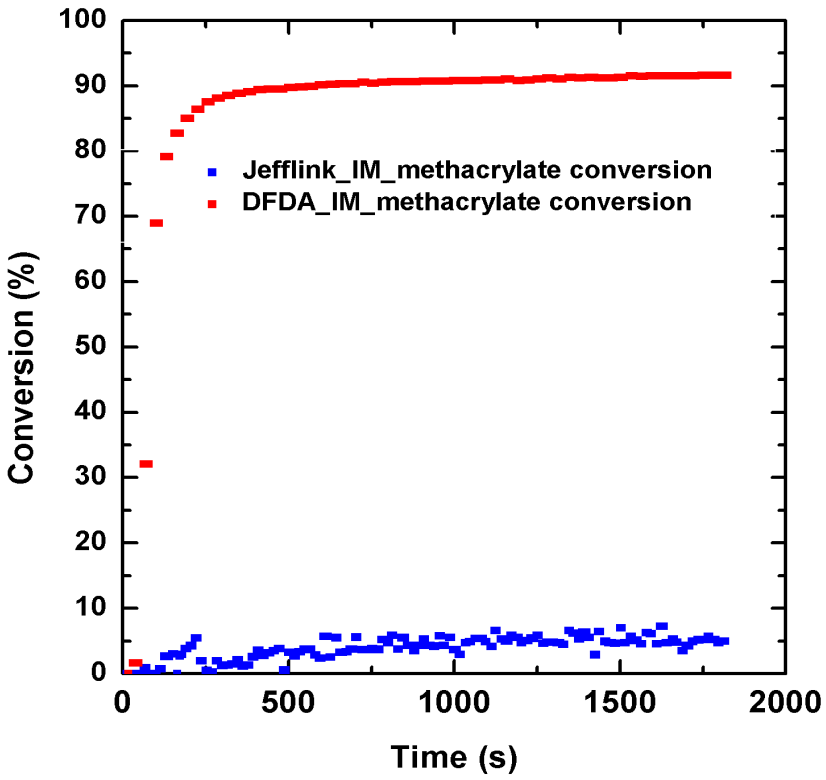


Figure 5. Methacrylate conversion vs. time of Jefflink/IM(blue) and DFDA/IM(red) systems.

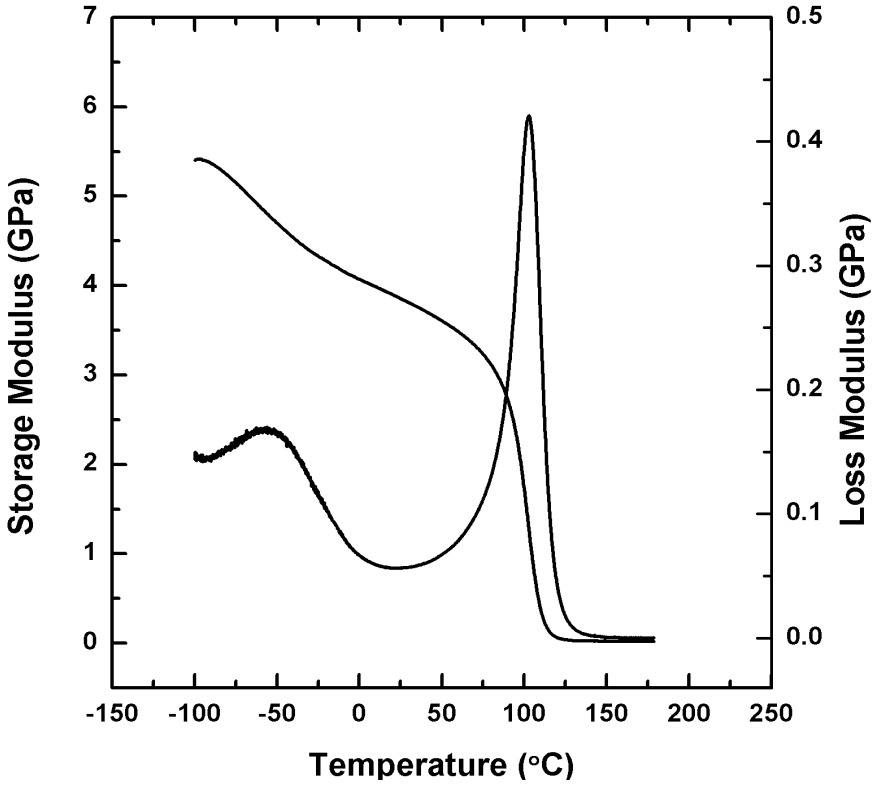


Figure 6. Storage modulus and loss modulus curves of DFDA/IM/DGEBA system.

Storage modulus (E′) and loss modulus curves (E″) as functions of time for DFDA/IM/DGEBA polymer system is given in **Figure 6**. The system exhibits a glass transition above room temperature (103 °C according to E″) and a secondary transition below -50 °C. By reacting secondary amine groups within the polymer system using DGEBA epoxy, the glass transition temperature was increased significantly. The single sharp loss modulus peak indicates that phase separation has not occurred in the cured polymer networks. The E′ curve below T_g shows that this polymer system has a high storage modulus of 3.9 GPa at room temperature. Previous work done by Hu et al has shown that DFDA amine curing agent impart a high glassy state storage modulus when cured into polymer systems [2]. The DMA data shows that this bio-based system has a comparable glass transition and a high storage modulus compared to traditional aromatic polymer systems. The results also suggest that isosorbide methacrylate and DGEBA are responsible for improved glass transition temperature. This will be further investigated by future studies.

4. CONCLUSIONS

A series of studies were preformed to understand the reactivity of amine with methacrylate to design formulations of prepared hybrid polymers. It was found that the reactivity of secondary amine and secondary amine formed with methacrylate is limited compared to that of primary amine with methacrylate. No crosslinked polymer was obtained from reacting DFDA with Isosorbide methacrylate at stoichiometry. To crosslink the system, DGEBA epoxy was used to blend DFDA with IM and to react secondary amine, which formed a material with a comparable

glass transition temperature of 103 °C according to loss modulus curve. This polymer systems possess a promising storage modulus (3.9 GPa). The study confirms that Aza-Michael addition reactions can be used effectively to form cross-linked networks. Unreacted secondary amines in such networks can react freely with epoxy monomers, which provides added control of network structure and composition. Michael addition schemes for network formation provides an effective platform for designing hybrid systems that incorporate bio-based building blocks to express specific behavioral characteristics. Future work will be performed to test the hypothesis that furan-based building blocks will provide higher storage modulus and better water barrier properties while isosorbide will provide higher glass transition temperature.

5. ACKNOWLEDGEMENT

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