

2-27-2021

An update on the future prospects of Glycerol Polymers

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Keywords

Glycerol, polymers, industrial applications, biodiesel

Disciplines

Polymer and Organic Materials

Comments

This is the peer-reviewed version of the following article: Goyal, Shailja, Nacú B. Hernández, and Eric Cochran. "An update on the future prospects of Glycerol Polymers." *Polymer International*, which has been published in final form at DOI: [10.1002/pi.6209](https://doi.org/10.1002/pi.6209). This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving. Posted with permission.

AN UPDATE ON THE FUTURE PROSPECTS OF GLYCEROL POLYMERS

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Abstract

Glycerol, a water-soluble polyol, is currently used in a wide variety of markets, e.g., as a sweetener in drinks, as an additive in the food and cosmetic industry, or as an antifreeze agent, to name a few. The blooming biodiesel production has created an excess supply of glycerol by-product. Researchers all around the world are actively exploring strategies to utilize this cheap and abundantly available biobased molecule. To date, glycerol-based polymers have only been examined extensively for use in biomedical applications, however, the use of biobased crude glycerol is nonviable for such applications due to the presence of impurities such as methanol and residual fatty acids from the biodiesel production process. Thankfully, the increased volumes of glycerol generated from biodiesel production have stimulated the research on its use in various other industrial applications such as the production of commodity chemicals, polymers, etc. In this article, we summarize some of the efforts to valorize glycerol for polymeric applications such as polyurethanes, polyhydroxyalkanoates, and adhesives.

Keywords: Glycerol, polymers, industrial applications, biodiesel

Introduction

Glycerol is a widely known biocompatible, non-toxic, and water-soluble polyol compound. It is currently used as a sweetener in drinks, solvent for food colorings, and as an emulsifier to improve the texture, viscosity, and water content of baked goods. Glycerol is also used as an anti-freeze agent, in cosmetics, it serves as a moisture-control reagent, emollient, and as a lubricant in oral and personal care products. It also finds its applications in pharmaceutical industries where it is used as a humectant and demulcent.^{1,2} Glycerol was traditionally derived from the saponification, hydrolysis, or transesterification of triglycerides and microbial fermentation.³ But in the last decade, biodiesel production emerged as a major source of crude glycerol. For every 100 pounds of biodiesel, 10 pounds of glycerol co-product is generated. Moreover, biodiesel production in the US escalated from 0.516 billion gallons in 2009 to 1.8 billion gallons in 2019, see **Figure 1**, owing to the increased global awareness for biofuels.⁴ This exponential growth has manifested a new era in glycerol research for large scale industrial applications. The “crude” glycerol by-product from the biodiesel industry contains a large number of impurities such as methanol, fatty acid methyl esters, soap, and water (85% by mass) along with glycerides, ash, free fatty acids (15% by mass).⁵ The purification process of glycerol is expensive which consequently escalates the economic stress on biodiesel production. Almost all crude glycerin is further processed and refined, but only vegetable source-based United States Pharmacopeia (USP) certified glycerol can be used for personal and oral care, and for human consumption uses. Glycerol based polymers exhibit excellent biocompatibility, hence polymers such as poly(glycerol ether), poly(glycerol carbonate)s, and dendritic hyperbranched glycerol-based polymers have been extensively studied till date for pharmaceutical applications such as drug delivery, tissue implants, and as an anti-bacterial agent.⁶ Howbeit the impurities present in glycerol makes it incompatible for such uses. Therefore, in the future, the major consumption of the abundant refined “crude” glycerin will be for the industrial production of chemicals and for novel uses in energy and polymeric materials production.

Various applications are being sought to valorize crude glycerol such as a fuel source, and to produce value-added chemicals. Glycerol is investigated as a feedstock for renewable energy generation.

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An excellent review paper by He *et al.* explains the numerous renewable energy generation processes from glycerol feedstock.⁷ Fermentation of crude glycerol as a carbon source via bacteria and/or yeast provides alcohols such as ethanol and butanol which are important biofuels. Due to advancements in fuel cell technology, the demand for hydrogen is soaring. Hydrogen production through steam reforming was comprehensively studied but the impurities present in crude glycerol deactivates and impedes the catalyst performance.⁸⁻¹⁰ Crude glycerol is also used as a co-digestion and co-gasification additive in biogas and syngas production. Nevertheless, both processes come with their own challenges. Higher glycerol addition (>4% v/v) to biomass for the co-digestion causes an imbalance in the digester, due to higher concentration of H₂S and volatile fatty acids (VFAs), and results in inefficiencies and system failure.^{11,12} Crude glycerol addition improves the yields of syngas and H₂ content but the performance of the process is highly dependent on optimization of the various parameters such as feedstock composition, residence time, temperature, pressure, etc. Moreover, higher crude glycerol feedstock (>20%) in the co-gasification process results in higher ash post combustion and blocks the gasifier grate. improves the yields of syngas and on the operation parameters.^{13,14}

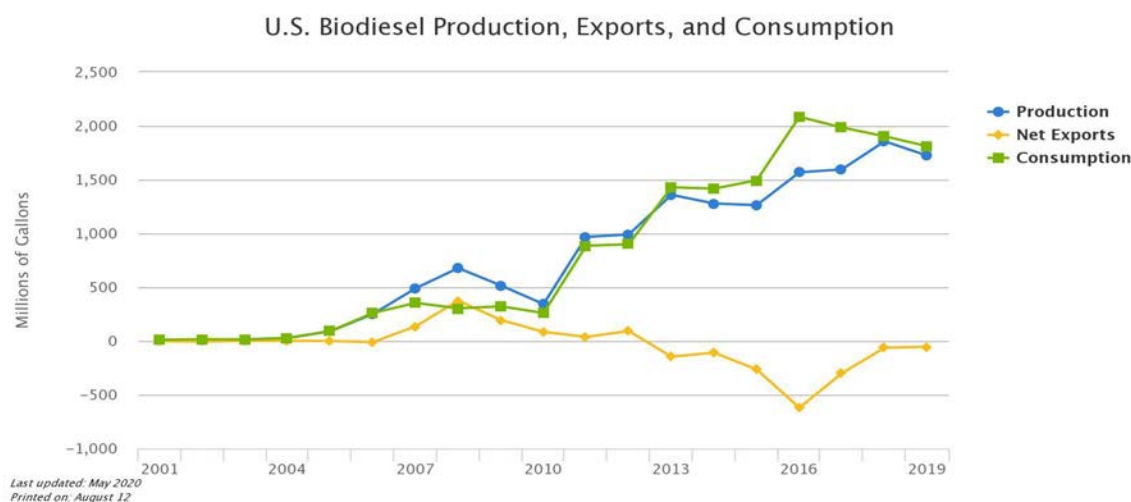


Figure 1. U.S. Biodiesel Production, Exports, and Consumption.

However, a new generation of state-of-the-art value-added chemicals produced from glycerol could be utilized for various commercial applications. Glycerol conversion to industrial chemicals can be achieved through catalytic pathways (such as oxidation, hydrogenation, etherification, etc.) or through biological pathways (aerobic and anaerobic catabolism). Several articles have summarized the numerous value-added chemicals that can be produced from glycerol.¹⁵⁻¹⁸ Biological pathways using different microorganisms (such as bacteria, fungi, and microalgae) and different reactions conditions (such as aerobic, anaerobic) can be used to produce chemicals such as 1,3 propanediol, glycerol carbonate, poly(hydroxyalkanoates), citric acid, and lipids. In addition, varied catalyzed chemical reactions generate products such as acrolein via dehydration, solketals via acetalization, and glycidol, acrylic acid, propionaldehyde, and propylene oxide via oxidation and reduction processes.¹⁹ The three hydroxyl groups on the glycerol molecule give endless opportunities to synthesize numerous chemicals with diverse functional groups that can then find use in a wide variety of applications. In addition, these chemical moieties unfold the possibility to use these now bioderived monomers in the synthesis of polymeric materials.

To date, much attention has been drawn to glycerol-based hyperbranched and dendritic polymers or block-copolymers for biomedical applications due to their excellent water solubility and biocompatibility.^{20,21} Carnahan *et al.* studied various polyglycerol ether aliphatic dendrimers containing glycerol and succinic acid,²² lactic acid,²³ or adipic acid.²⁴ These involved a divergent route (from the core

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to the surface) for synthesizing the dendrimers by alternating repetitive reactions of cis-1,3-o-benzylidene glycerol with the respective acid component followed by the hydrolysis of the acetal functional group. The two primary alcohols of the glycerol were protected by forming the ketal functional group, thus allowing the remaining hydroxyl group to be functionalized independently. Despite tremendous functionalization capabilities, glycerol polymers have been overlooked for industrial applications and material characterization by polymer scientists till date. The literature majorly focuses on glycerol dendrimers and block copolymer synthesis. There is an immense potential to study glycerol-based condensation polymers and diblock copolymers as tougheners and compatibilizers for polymer matrices, additives and tackifiers for adhesives, and / or hygroscopic coatings. Owing to the now available economic and ecological incentive, researchers have embarked to search for novel applications of these glycerol-based polymers. In 2016, poly(monostearoyl glycerol-co-succinate) polymer was recently patented as an additive to enhance topical absorption of personal care products.²⁵ Valerio et al. demonstrated the application of glycerol polyesters with succinic acid and maleic anhydride such as [poly(glycerol succinate-co-maleate), PGSMA] to toughen polylactic acid (PLA). The reactive extrusion resulted in the formation of PLA-g-PGSMA graft copolymers and improved the tensile toughness of neat PLA by about 392%.^{26,27} Further, PGSMA/PLA and poly(butylene succinate) 35/40/25 blend resulted in mechanical properties such as tensile strength of 33.8 MPa, and notched Izod impact of 159 J/m which is comparable to some commercial polypropylene products.²⁸ Recently, Wang et al. reported promising conclusions that poly(glycerol maleate) (PGM) degrades rapidly in aqueous environments. They found PLA degrades less than 3% over 56 days in RO, tap and artificial sea water at 25°C. However, PGM degrades completely with 100% mass loss in about 35 and 28 days in tap and artificial seawater.²⁹ Hsieh et al. further elicited the application of microbeads in personal care products as a replacement for non-biodegradable polymer microbeads such as polyethylene, polypropylene and poly(methyl methacrylate) etc.³⁰ They outline complete degradation of these PGM microbeads in alkaline solution (pH 10) in about 45 mins, 59% and 36% degradation in acidic solution (pH 4) and synthetic sea water after 30 days. The authors suggest the promising biodegradable alternative presented in the literature, PLA microbeads, only degraded in alkaline solution in their experiments. Hence PGM may be more affordable and better degradable options to petroleum based or PLA based microbeads. As stated earlier, multiple hydroxyl groups of glycerol could be instrumental to future biobased polymeric material design. Hastenreiter et al. synthesized polyester thermoset resins with glycerol and lactic acid and then end-functionalized them with methacrylic anhydride. The thermoset material had a glass transition temperature around 44°C, tensile modulus of 3.76 GPa, tensile strength of 11.08 MPa and showed signs of macro-scale surface degradation on a soil burial test.³¹ Thus glycerol based polymers illustrate a wide possibility for functionalizations and hence easier tunability for various polymer synthesis chemistries and matrix compatibility. In addition, ether and/or ester bonds would render the polymers biodegradability through hydrolysis. Our research group recently patented the acrylated glycerols which have the potential for applications as a biobased alternative for hard, rigid thermoplastic and thermoset materials.³² Acrylated glycerol is synthesized in a one-pot reaction yielding multifunctional monomers which form soft gel on polymerization reaction. These acrylate glycerol polymers may be used as asphalt rubber modifiers, adhesives, or an additive in a fracking fluid for oil fracking.

There have also been various reports of glycerol linear and hyperbranched diblock copolymers in the literature. Wurm *et al.* demonstrated the synthesis of double hydrophilic diblock copolymers of linear and hyperbranched glycerol with poly (ethylene oxide) (PEO),^{33,34} as shown in **Figure 2**. Cunningham et al. depict the aqueous RAFT emulsion polymerization for diblock nanoparticle polymer synthesis with hydrophilic glycerol monomethacrylate and hydrophobic benzyl methacrylate monomers. Their motivation was to assess the efficacy of these nanoparticles as Pickering emulsifiers.³⁵ This presents an opportunity for various glycerol polymers as the hydrophilic block in emulsion polymerization to substitute the traditional hydrophilic blocks such as acrylic, methacrylic and acrylamide in core-shell polymer synthesis. Hydrophilic and hydrophobic monomer combination core-shell polymers are also used to produce responsive materials for controlled release and thermal sensitivity applications.³⁶

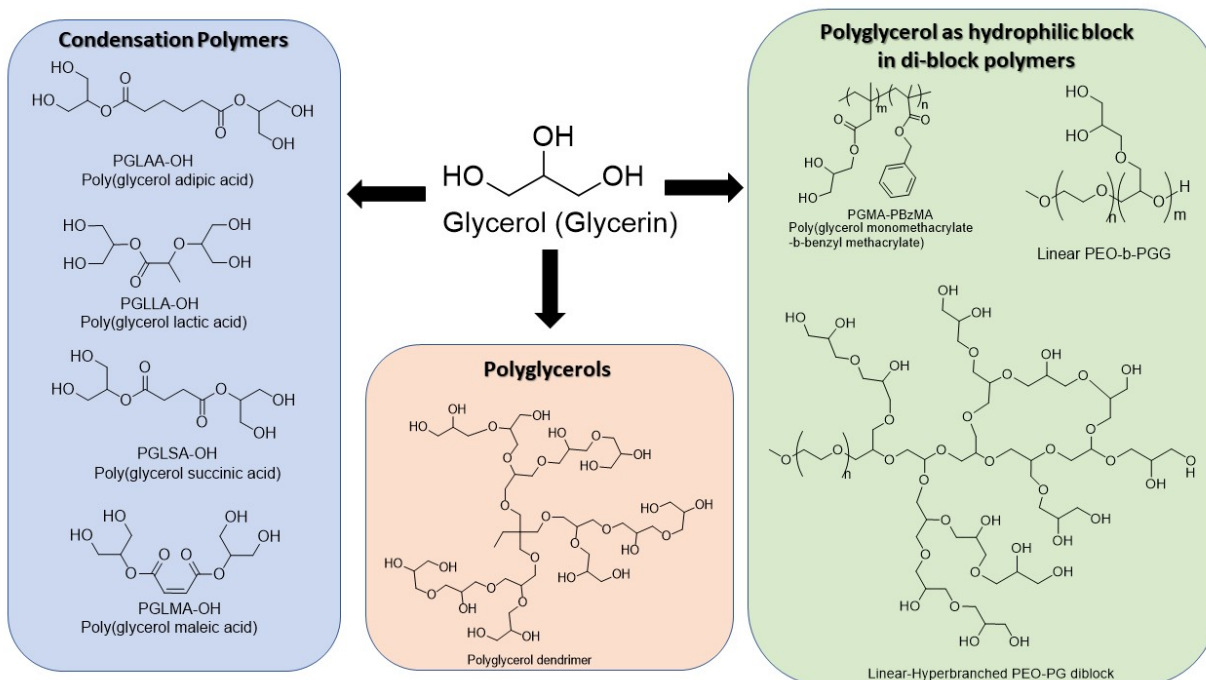


Figure 2. Various synthesis routes for glycerol polymers

Another advancement of glycerol research, for high volume polymer material applications, has been in the production of polyurethane foam and polyhydroxyalkanoates. Polyurethane polymers (PUs) are composed of carbamate (urethane) moieties synthesized by reaction of isocyanate and polyols by catalyst of ultraviolet light activation. Higher functionality of polyols ($f > 3$) result in increased cross linking and rigid PUs while lower functionality polyols, such as glycerol ($f = 3$), dipropylene glycol ($f = 2$) result in flexible PUs.³⁷ Due to the intense ability to tune mechanical and thermal properties of PUs based on the choice of building block, PUs find wide range of applications as soft thermoplastics for keyboard, mobile protectors, extruded film and sheet applications to more rigid PUs as thermal and sound insulators, furniture, automotive interior parts. Due to the widespread applications of PUs, there is an intense focus to develop biobased and/or biodegradable PUs.³⁸ Crude glycerol has been widely studied as the precursor for PUs,³⁹⁻⁴¹ even for specific applications such as thermal energy insulators,^{42,43} waterborne films,⁴⁴⁻⁴⁶ and sound absorbers.⁴⁷ Crude glycerol is typically heated under vacuum at temperature (150-200°C) and a condenser for 2-5 hours to synthesize polyols. These crude glycerol-based polyols are then mixed with diisocyanates in the presence of catalyst at room temperature to generate PU foams. Li's research group has extensively studied polyurethane foam production from glycerol polyols.^{48,49} They discovered that certain organic impurities such as free fatty acid (FFA), fatty acid methyl esters (FAMES), and glycerides improved the biomass liquefaction process to derive polyols and PU foams. During the polyol production process from crude glycerol, esterification and transesterification reactions between glycerol and FFAs and FAMES respectively results in monoglycerides and diglycerides with long fatty acid ester chains.⁴⁸ They reported that these branched fatty acid ester chains hindered arrangement of urea hard segments and stabilized the bubbles during foaming process. The esterification and transesterification reactions between glycerol and acid groups results in lower hydroxyl numbers and higher molecular weight polyols. Commercial produced polyols typically have hydroxyl numbers between 34-800 mg KOH/g and average molecular weight (M_w) between 200-1000 g/mol. In a typical study, crude glycerol with over 45% organic impurities (mainly FFA and FAMES) manifested hydroxyl numbers less than 800 mg KOH/g. M_w of polyols from crude glycerol ranged from 472 g/mol (40% of FFA and FAMES) to 1013 g/mol (80% FFA and FAMES) making it suitable to produce rigid or semi-rigid PU foams.⁵⁰ Li's group also explored the application of crude glycerol derived PU as a wood adhesive. The shear strength obtained from crude glycerol PU was about 36.8 MPa,

comparable to that of the commercially available PU wood adhesives (J.E. Moser's Wood Glue: 30.2 MPa, Sikaflex PU adhesive: 37.7 MPa).⁵¹ They also demonstrated the use of crude glycerol as a solvent in the traditional liquefaction process of lignocellulosic biomass to produce polyols in lieu of petroleum-derived polyhydric alcohols. The properties of the polyols and PU foams produced with crude glycerol solvent were comparable to the petroleum solvent-based biomass liquefaction processes.⁵² In addition, glycerol levulinate ketals (GLK) have been reported to synthesize rigid PUs with compressive strength up to 197 kPa.^{53,54} High yields of GLK obtained (up to 97.2%) by reaction of alkyl levulinate (obtained from one-pot synthesis of biomass) and glycerol are promising PUs precursors obtained from bio sourced building blocks. Due to the versatility of glycerol functionalizations there is immense potential for synthesis of custom PUs.

In addition to the PU foams, recent literature also reports the production of polyhydroxyalkanoates (PHA) from crude glycerol. PHA are natural biodegradable linear polyesters of 3, 4, 5 & 6 hydroxy acids produced by a variety of microorganisms through fermentation. PHAs are highly crystalline polymers with typically high melting temperatures 140-180°C and mechanical properties like polypropylene. As these are produced in the intracellular granules inside cells of microorganisms, these are truly biodegradable polymers and have no toxic effects in living organisms.⁵⁵ The applications of PHAs are still limited due to high costs of production. Crude glycerol has emerged as promising carbon source for the fermentation process to produce PHA biopolymers to reduce the costs as raw material accounts for 40-48% of PHA production cost.⁵⁶ Glycerol is fed as the carbon source in cultured batch reactors along with appropriate quantities of nutrients for microbial growth in aerobic conditions. Several studies have been conducted with different microorganisms to test the efficacy of the process.⁵⁶⁻⁵⁹ **Figure 3** gives the typical schematic for PHA production from crude glycerol. Moita *et al.* reported achieving a higher Polyhydroxybutyrate(PHB) content (47% cell dry weight) with crude glycerol when compared to the PHB content obtained using the wastes from other sources such as wood mill, paper mill, etc.⁶⁰ Most complex wastes are pre-fermented to increase the volatile fatty acid (VFA) content. VFAs are the primary precursors to produce PHAs, thus they are essential to obtain higher PHA contents. The PHA yield obtained from crude glycerol without the pre-fermentation process (0.32 g COD HB/g COD crude glycerol) is comparable to those obtained from other waste sources after pretreatment (0.08-0.58 g COD PHA/g COD real waste) which would make the overall process more efficient.

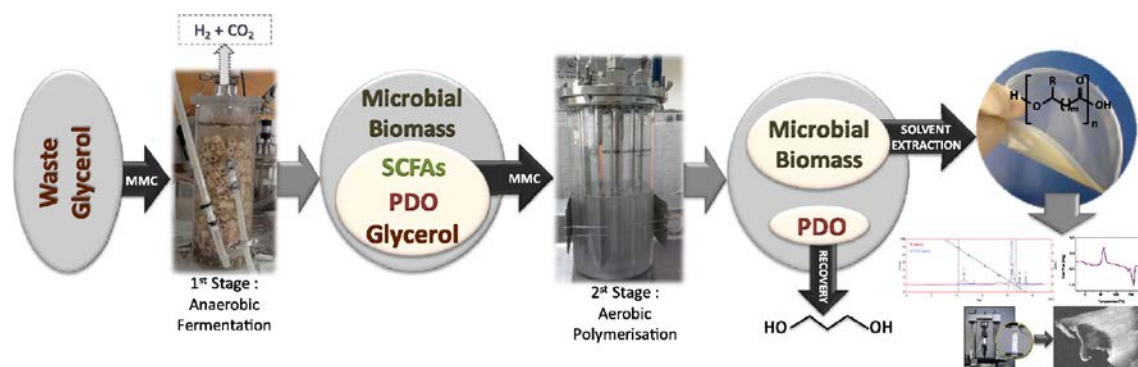


Figure 3. Schematic representation of the valorization of waste glycerol via microbiological process to synthesize PHAs. Reprinted from [30], ©(2018), with permission from Elsevier.

In the past decade, our research group, at Iowa State University, has concerted efforts to systematically study diverse methods for the synthesis of glycerol monomers and the characterization of various glycerol-based polymers for industrial applications such as pressure sensitive and wood adhesives. Our group is focused on innovative ways to synthesize glycerol polymers with controlled molecular weight (to achieve desirable mechanical and thermal properties) with scalable experimental methods. Forrester *et al.* devised a family of hyperbranched thermoplastic acrylic polymers from glycerol multi acrylate monomers through an esterification process.⁶¹ We were able to synthesize glycerol acrylate monomers through a solvent-free Fisher esterification process by combining crude or analytical grade glycerol with acrylic acid in the

presence of a catalyst and a radical inhibitor. The monomer composition consisted of a mixture of mono-, di- and tri-acrylated glycerol which was highly susceptible to crosslink and undergo gelation upon polymerization through the multiple vinyl groups. Nonetheless, the polymers were synthesized through a controlled Radical Addition Fragmentation Transfer (RAFT) polymerization technique. In RAFT polymerization, majority of the chains are initiated by the chain transfer agent (CTA) and thus are transformed into a dormant form. This limits the crosslinking of these monomers to form macrogels at lower conversions and promotes branching. The polymers had molecular weights higher than 1MDa with glass transition temperatures (T_g) ranging from $-22\text{ }^\circ\text{C}$ to $0\text{ }^\circ\text{C}$. The properties of these polyacrylated glycerol polymers (PAG) were then explored for water-based sprayable wood composite adhesive applications. The shear test results indicated that the plywood constructed from only PAG (10MPa) has nearly the same shear strength as pure maple wood (13 MPa). These polymers, nonetheless, were not suited for wet applications. However, with the addition of 10-20% polymeric methyl diphenyl diisocyanate (pMDI), PAG can give similar wet and boiled water strength as compared to 100% pMDI adhesive boards as shown in Fig. 4. PAG and pMDI form urethane linkages which strengthen the polymer adhesive strength and reduce water affinity. PAG has emerged as a bio-sourced wood adhesive at reduced costs ($<\$1.00$ per lb vs. $\$2.00$ per lb) and environment-friendly synthesis methods as compared to the traditional pMDI adhesives.

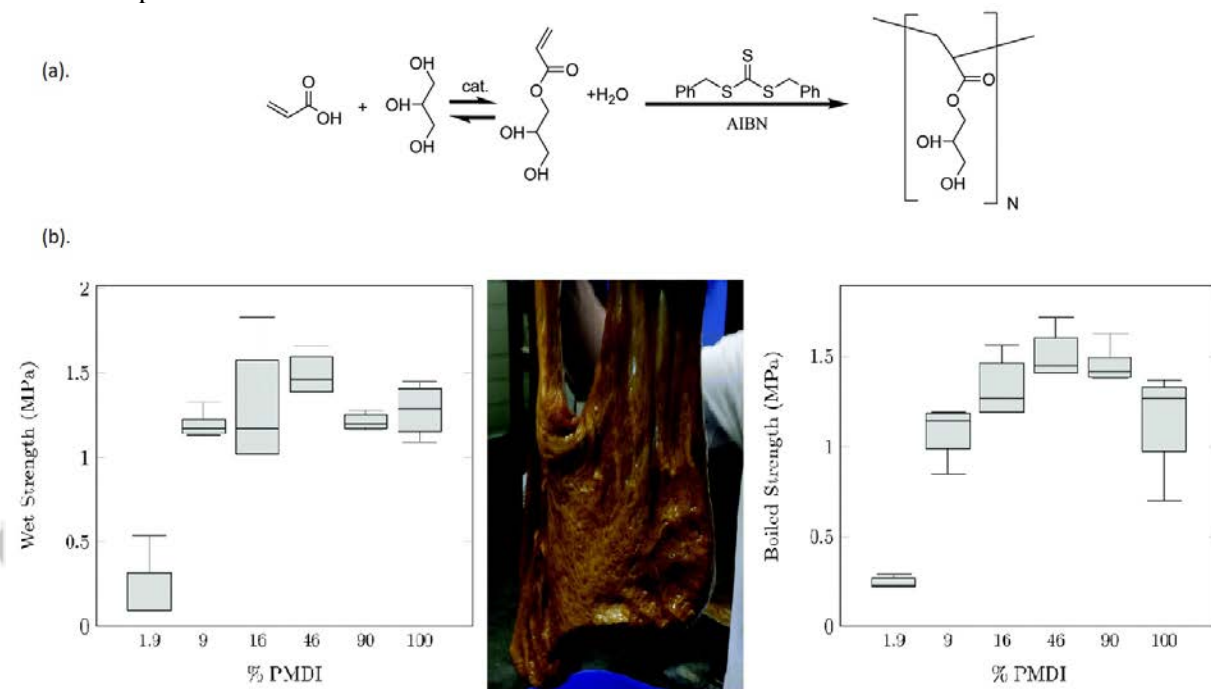


Figure 4. (a). Simplified synthetic route to produce PAG from crude glycerol. (b). Wet strength of plywood samples that have been soaked in water at various loadings of PAG1.3-C/pMDI. (Middle) Image of the scale-up reaction of PAG1.3-C. This represents 1 kg of material. (Right) Plot showing the strength of samples that have been boiled in water. 100% PMDI control shown in both plots. Republished with permission of the Royal Society of Chemistry, from [33]; permission conveyed through Copyright Clearance Center, Inc.

On a different approach, we explored monofunctional linear acrylate polymers from glycerol. The primary and secondary alcohol groups were protected to a ketal functionality by the reaction of glycerol with various ketones. The alcohol group on the ketal was esterified with methyl acrylate and methyl methacrylate as shown in **Figure 5**. The linear RAFT polymers synthesized had different pendant side chain groups and their effect on thermal and rheological properties was studied. The rigid side-chain groups such as cyclo ring structures reduced mobility and thus resulted in higher T_g as compared to alkyl side chain groups. The glass transition temperatures of these polymers were in the range of -11 to 40°C .

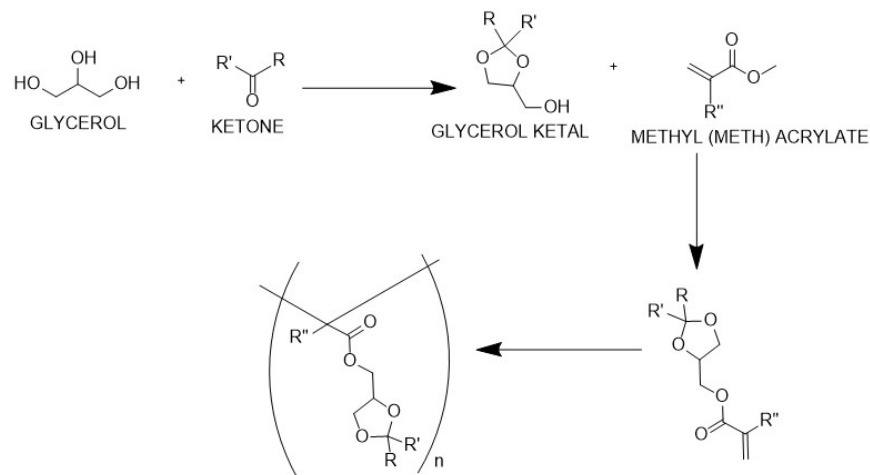


Figure 5. Synthesis and characterization of various glycerol ketal side chains polymers.

The low T_g of these polymers excited us to study their properties as a block copolymer and we discovered these could prove to be a suitable replacement for petroleum-based pressure-sensitive adhesives (PSA). Lin *et al.* synthesized triblock copolymers of solketal acrylate and isobornyl acrylate by RAFT polymerization and confirmed their entanglement behavior and spherical morphology through SAXS. An addition of benzoflex plasticizer yielded polymers suitable for removable PSA and high shear PSA applications and they do not require an additional tackifier for bonding strength. Further thermal and mechanical characterizations of these polymers are currently in progress. But our initial findings have established evidence for the endless possibilities of glycerol-based polymers for high volume industrial applications and opening the door to an almost untapped research field.

Conclusion

Transportation sector generates the largest share of greenhouse gas (GHG) emissions (about 28.2% of the total GHG emissions in 2018).⁶² The advent of electric cars is much debated to replace traditional liquid fuel vehicles to minimize GHG emissions but the limited miles on a full charge, recharging time, limited infrastructure, and consumer will to switch purport a lot of challenges for electric vehicles. The innovation in the fuel sector to generate zero waste biodiesel by valorizing crude glycerol will be crucial in decarbonizing the transportation sector.^{63,64} Glycerol has thus emerged as a cheap biobased byproduct of biodiesel production and offers the potential of synthesizing a plethora of chemicals and polymers through its three hydroxyl groups. The multiple functionalities of glycerol will offer us numerous handles to tweak thermal and mechanical properties, hydrophilicity, polarity, etc. of the polymeric materials produced from it. Glycerol based hyperbranched and dendritic polymers have been traditionally studied for biomedical research due to their biocompatibility and hydrophilicity. In the last 5 years, applications of glycerol for polymer synthesis such as polyurethane foams and polyhydroxyalkanoates have started to be widely studied. In addition, our research group, at ISU, has recently started exploring synthetic polymers and their mechanical and thermal properties from glycerol for industrial applications. We demonstrated the synthesis of glycerol acrylate multifunctional polymer through controlled radical polymerization technique, RAFT, for industrial wood adhesive applications. We further investigated the use of diblock copolymers based on ketal acrylate monomers from glycerol monomer precursor exhibit rheological properties which indicate possible applications as a pressure-sensitive adhesive. We believe that glycerol-based polymers may be critical in discovering the new generation of environment-friendly bioderived materials. However, their

mass adoption will depend on the availability of crude glycerol as raw material and the sustainability of the biodiesel production.

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