

Natural Oil Polyol of High Reactivity for Rigid Polyurethanes

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ABSTRACT

A new tri-functional natural oil-derived polyol has been developed. Its hydroxyl number ranges from 320 to 350 mg KOH/g. The polyol contains both primary and secondary hydroxyl groups with demonstrated ability to rapidly build polyurethane cross-linked networks. It is completely miscible with a wide variety of natural oil polyols, petrochemical-based polyether polyols, and hydrocarbon blowing agents. This excellent miscibility together with its low viscosity (2,000-3,500 cP at 25°C) and good reactivity enables manufacture of polyurethane rigid foams with increased biobased content.

INTRODUCTION

Polyurethane rigid foams are widely used as insulation and structural materials for construction, transportation, decoration, and appliances. Those foams account for almost one-third of the polyurethane market. Out of annual 2.8 billion lbs of North American polyol market^[1], approximately 1.3 billion lbs of polyols are used for manufacturing polyurethane rigid foams. These cellular materials are made by reacting polyols with polyisocyanates with the proper amount of catalysts, additives, and blowing agents. As a cross-linked material, the rigidity of polyurethane foams is closely associated with the formation of cross-linked structures and urea linkages. In general, preparation of highly cross-linked polyurethane material requires a reactive polyol that has a relatively high hydroxyl number ranging from 200 to 800 mg KOH/g and high functionality (usually from 3 to 5). Typical commercially available polyether polyols that are used for making rigid polyurethane foams are triols and higher functional polyols with hydroxyl numbers from 300 to 500 mg KOH/g. Propylene oxide, ethylene oxide, alkyl phenol, and formaldehyde are used for making most polyether polyols that are suitable for rigid polyurethane foams. These raw materials are derived from non-renewable feedstock.

The interest in using biobased polyols, especially natural oil polyols, in the manufacture of polyurethane products has increased significantly in the recent years^[2-6,7]. The most promising natural oils for the industrial development of biobased polyols are soybean oil, castor oil, palm oil, and canola oil. Commercially available natural oil polyols from BioBased Technologies[®] (Agrol[®]) as well as Urethane Soy Systems Company, Cargill, Dow, BASF, and Bayer are used for making polyurethane foams for automotive, furniture, spray insulation and other industries. These polyol producers and the manufacturers of polyurethane products are driving the incorporation of natural oil polyols into polyurethane products and the creation of sustainable materials. Optimistic industrial estimation suggests that consumption of soybean oil polyols could reach 650 million lbs by 2009, of which potential demand from rigid spray foam alone could be up to 100 million lbs.^[1, 5] However, it was reported that only 20 million lbs of soybean oil polyols were produced in the United States in 2006^[5]. In order to increase the substitution level of natural oil polyols, it is oftentimes required that natural oil polyols have good compatibility with the conventional petrochemical-based polyurethane systems.

Agrol[®] polyols have wide acceptance in the polyurethane spray foam insulation, automotive, and carpet industries. However, from the rigid foam market segment there is still a strong customer demand for natural oil polyols of required reactivity and hydroxyl number, while maintaining high biobased content. Agrol Diamond[™] is a new natural oil polyol from BioBased Technologies[®]. This polyol has recently launched in response to such customer demand for polyurethane rigid foam markets. In this paper, the technical characteristics of Agrol Diamond[™] will be discussed.

EXPERIMENTAL

Raw Materials

Agrol[®] 3.0, Agrol[®] 3.6, Agrol[®] 4.3, Agrol[®] 5.6, and Agrol Diamond[™] are commercially available from BioBased Technologies[®], LLC.

Polymeric diphenylmethane diisocyanate (PMDI; Mondur[®] MR-Light, NCO% = 31.5, functionality = 2.8, viscosity = 200 cP at 25 °C, equivalent weight 133) was purchased from Bayer Materials Science NAFTA (Pittsburg, PA).

DABCO 33-LV[®] (Air Products, Allentown, PA) is the catalyst that was used for the investigation on reactivity of polyols.

Chemical Analysis

Agrol Diamond[®] was analyzed by using the American Oil Chemists' Society (AOCS) Official Process of analysis: Cd 3d-63 for acid number; Cd 13-60 for hydroxyl number; Ja 10-87 for viscosity; Tb 2-64 for water content, and Td 1a-64 for color, Gardner 1963 (Glass Standard).

Biobased content was determined using ASTM-D6866 at Beta Analytic Inc. (Miami, FL).

Brookfield Viscosity Test

The Brookfield Viscosity Test (BVT) method was used to characterize the reactivity of the natural oil polyols with polyisocyanates. The BVT method measures viscosity increase with the reaction time after mixing a polyol with liquid PMDI. To determine the reactivity characteristics of a polyol, a polyol or a polyol blend (100 g) was placed into a 250 ml wide mouth plastic cup. Catalyst was added at up to 0.2% based on the polyol weight. The calculated amount of PMDI was introduced, mixed mechanically for 30 seconds, then the cup was placed on the viscometer and the viscosity was recorded as the reaction progressed. The data was plotted to give a BVT Reactivity Curve for the test. Onset gelation time was recorded as the time at which viscosity reached 5,000 cP on the viscosity-curing time plot. Gelation time was recorded as the time when viscosity reached 30,000 cP on the viscosity-curing time plot. Percentage in the present paper refers to the weight percent based on the total mass of polyols.

Polyol Miscibility Test

The miscibility tests were conducted by mixing Agrol Diamond[™] with conventional polyether polyols or other chemicals in a metric scale cylinder. The cylinder was then placed in the oven at 60 °C for 12 hours and removed from the oven and brought to room temperature over 48 hours. The volume of each phase was measured. The determined miscibility refers to the solubility of Agrol Diamond[™], which was calculated based on the volume ratios.

Mechanical Properties Tests

Polyurethane foams were aged two weeks at ambient temperature prior to conducting the tests. Density was measured in compliance with ASTM D1622; tensile strength and elongation were measured in compliance with ASTM D1623; compressive strength was measured in compliance with ASTM D1621.

RESULTS AND DISCUSSIONS

Agrol Diamond[™] is an amber-colored liquid that contains reactive hydroxyl groups (Table 1). The biobased content of Agrol Diamond[™] is 86 %. In comparison with other commercially available Agrol[®] polyols of high functionality (such as Agrol 5.6 and Agrol 7.0), the viscosity of Agrol Diamond[™] is significantly lower. With increasing temperature, the viscosity of Agrol Diamond[™] (Figure 1) decreases rapidly. At 55 °C, viscosity of Agrol Diamond[™] is 130 cP, inbetween the viscosities of Agrol[®] 3.0 (115 cP) and Agrol[®] 5.6 (430 cP). Polarity and molecular weight are two major factors that affect the viscosity of polyols. The typical hydroxyl number of Agrol[®] 3.0 is 103 mg KOH/g, which is almost 1/3 of that of Agrol Diamond[™], explaining the relatively low viscosity of Agrol[®] 3.0. The molecular weight of Agrol Diamond[™] is in the range of 510-560 Daltons, which is significantly lower than that of Agrol[®] 5.6, a polyol with molecular weight of 1950-2000 Daltons. Since Agrol Diamond[™] is more polar and has lower molecular weight than Agrol[®] 5.6, it possesses moderate viscosity.

Table 1 Characteristics of Agrol Diamond™

Property	Value
OH number (mg KOH/g)	320-350
Viscosity (cP at 25 °C)	≤ 3500
Water content (%)	≤ 0.1
Acid number	≤ 1
Color (Gardner color)	5
Nominal Functionality	3
Equivalent weight (Daltons)	160-175
Vapor pressure (mm Hg / 175 °F)	0.5
Specific gravity (25 °C)	1.01-1.03
Biobased content (%)	86 ± 3

It is known that isocyanate reacts faster with primary hydroxyl groups than with secondary hydroxyl groups.^[8] Agrol[®] polyols from Agrol[®] 2.0 to Agrol[®] 7.0 have only secondary hydroxyl groups while Agrol Diamond™ contains both primary and secondary hydroxyl groups. The presence of these primary hydroxyls in Agrol Diamond™ should contribute to the reactivity of this polyol and the blends of Agrol[®] polyols with it. Figure 2 shows a series of BVT reactivity curves on the blends of Agrol[®] 4.3 with Agrol Diamond™. As it can be seen, the viscosity increases much faster when more Agrol Diamond™ is added to Agrol[®] 4.3. These results are also presented in Figure 3 in terms of gelation time and onset gelation time in order to characterize reactivity of these polyols. The longer the onset gelation time, the slower the polyol reacts with the isocyanate and slower to start building the rigid polyurethane network. Onset gelation time is related with the intrinsic nature of the polyol such as primary hydroxyl or secondary hydroxyl groups and the hydroxyl numbers. Gelation time derived from BVT measurements reflects the total reaction time. A longer gelation time requires a longer process cycle time to complete the preparation of the polyurethane materials. The difference between the gelation time and the onset gelation time (Δt) can be used to characterize how fast a rigid polyurethane network can be built. A small Δt value means a rigid polyurethane network is built quickly, and therefore, a polyurethane end product may be produced with short in-mold or tack-free time. Δt is related with the properties that attribute to the rigidity of a cross-linked network, for example, functionality and interchain molecular weight of the polyol.

Figure 3 shows that gelation time is dramatically decreased with increasing concentration of Agrol Diamond™ in Agrol[®] 4.3. When only 10 % of Agrol Diamond™ is used, the gelation time is reduced from 149 min to 57 min; correspondingly, onset gelation time decreases with the increasing concentration of Agrol Diamond™. More importantly, Δt is also reduced from 63 min to 23 min. Further increasing the amount of Agrol Diamond™ to 20, 30, 40, and 50 % reduces Δt values to 11, 6, 4, and 3 min, respectively. Pure Agrol Diamond™ shows a Δt of less than 1 min. Therefore, Agrol Diamond™ enhances both the reactivity and the rate at which the rigid polyurethane network is formed.

DABCO 33-LV[®] is a strong multi-purpose gelation catalyst that increases the reaction rate between hydroxyl and isocyanate groups. Figure 4 shows the effect of the catalyst on the gelation time and onset gelation time of the 80/20 blend of Agrol[®] 4.3 and Agrol Diamond™. As it can be seen, increasing catalyst concentration linearly reduces gelation time, onset gelation time, and Δt . Results shown in Figure 5 demonstrate the effect of Agrol Diamond™ on Δt with and without catalyst. With 10 % Agrol Diamond™, Δt is reduced from 63 min to 23 min and then further reduced to 5 min after adding 0.2 % catalyst. Δt values are further reduced to 2 min when 30 % Agrol Diamond™ is combined with 0.2 % of catalyst. The functionality of Agrol Diamond™ is 3, which is lower than that of Agrol[®] 4.3. This causes the average functionality of the system to be slightly lower than that of Agrol[®] 4.3 when Agrol Diamond™ is added. Given this lower functionality; one may conclude that

the increased reactivity and the rate of building the polyurethane network can be attributed to the primary hydroxyl groups and relatively low molecular weight of Agrol Diamond™.

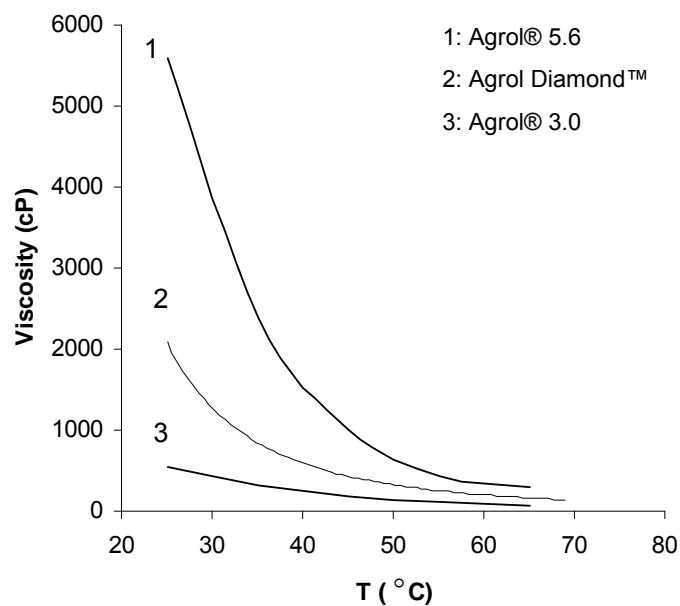


Figure 1 Viscosity of Agrol® polyols

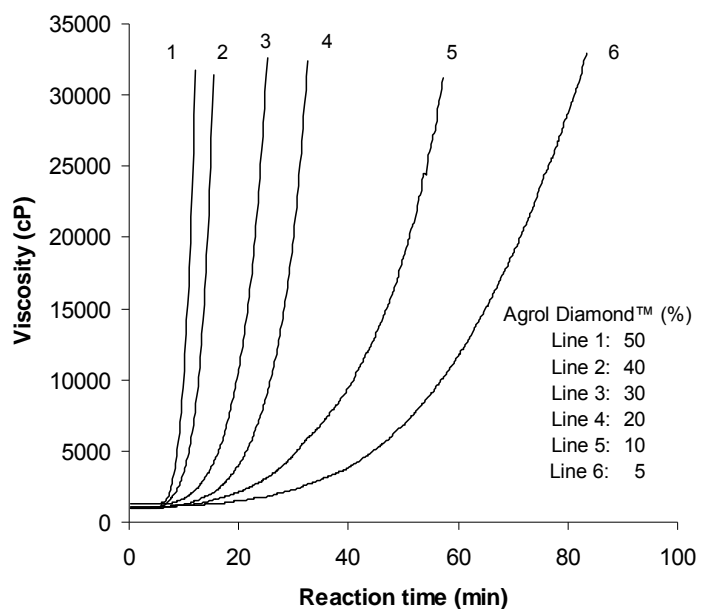


Figure 2 BVT Reactivity test results for Agrol® 4.3/Agrol Diamond™ blends without catalyst

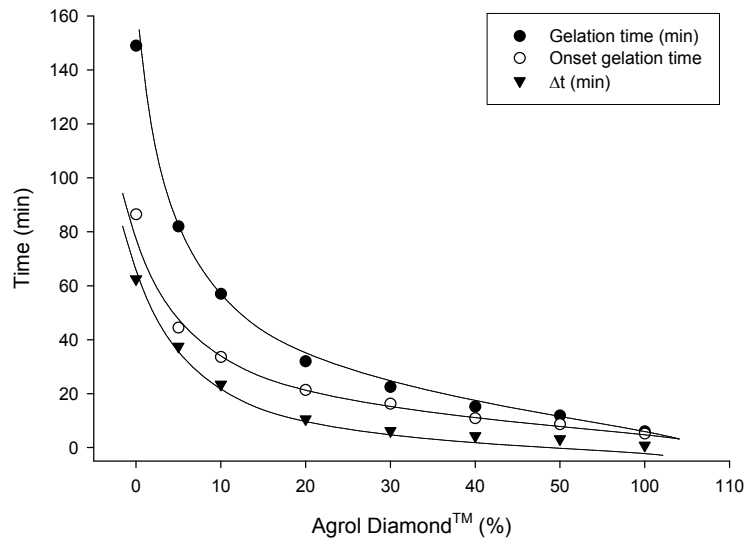


Figure 3 Gelation time and onset gelation time for Agrol® 4.3/Agrol Diamond™ blends without catalyst

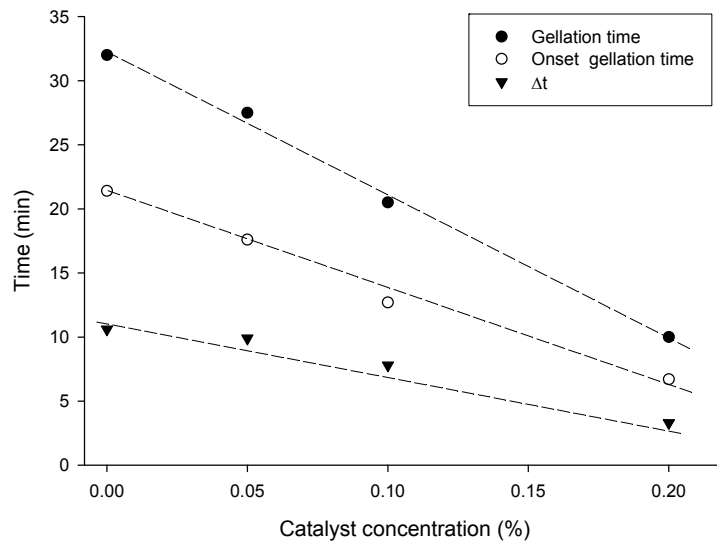


Figure 4 Effect of catalyst concentration on reactivity of the 80/20 Agrol® 4.3/Agrol Diamond™ blend

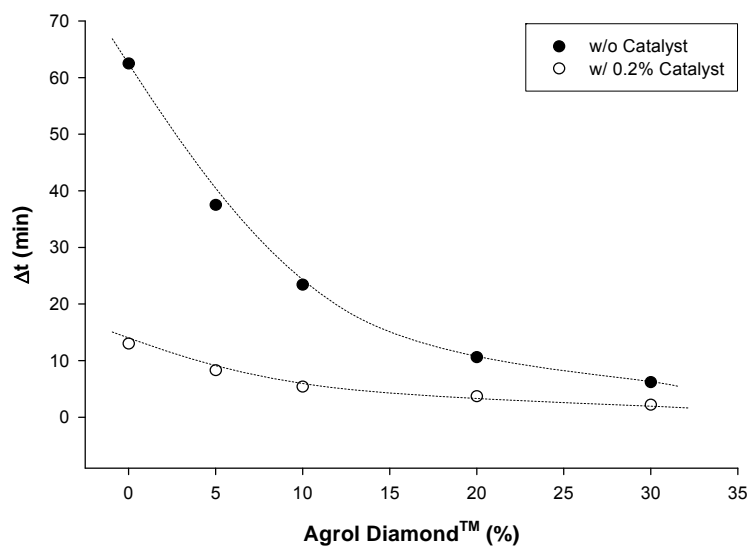


Figure 5 Δt for Agrol® 4.3/Agrol Diamond™ blends with and without catalyst

Miscibility of Agrol Diamond™ with other components of polyurethane systems is very critical for developing rigid polyurethane formulations. Pechar *et al.*^[9] reported that soybean oil polyol (hydroxyl number 117 mg KOH/g; supplied by BioBased Technologies®) showed good homogeneity when mixed with Voranol 4701, a petroleum-based polyether polyol (OH number 34 mg KOH/g, functionality ~2.5, and ~74% ethylene oxide end-capped; supplied by Dow) based on results of Dynamic Mechanical Analysis. Guo *et al.*^[10] reported that cyclopentane was more compatible with soy-based polyol than with poly (propylene oxide)-based polyols. Table 2 provides a list of selected natural oil polyol types and conventional polyether polyols that showed complete miscibility with Agrol Diamond™ as determined by visual observation. In addition to being completely miscible with these polyols, Agrol Diamond™ also demonstrates excellent miscibility with n-pentane, cyclopentane, and hexane in our experiments. These hydrocarbon chemicals are typical blowing agents for producing polyisocyanurate rigid foams. The excellent compatibility of Agrol Diamond™ with other polyols and hydrocarbon blowing agents opens up an opportunity for the preparation of rigid foams with increased biobased content.

Table 3 provides comparative data on the maximum attainable biobased content and corresponding compressive strength of water-blown polyurethane spray foam systems. The open-cell pour-in-place foam systems (nominal density of 1.6 pcf; formulations 1 and 2) were made with Agrol® 5.6 or Agrol Diamond™ to achieve similar foaming characteristics (cream time 14-16 sec., tack-free time 85-95 sec., and gel time 38-42 sec.). Compressive strength values of the two formulations were also found to be similar. However, formulation 2, which was made with the use of Agrol Diamond™, has significantly higher biobased content of 50%. Similar results were obtained in the case of closed-cell foam. Formulation 3 contains Agrol 5.6 and formulation 4 contains a combination of Agrol® 5.6 and Agrol Diamond™, yielding polyurethane foam with nominal density of 1.7 pcf. Both formulations produce similar foaming characteristics (cream time 4-6 sec. and rise time 18-22 sec.) and compressive strength values. Similar to the open cell foam, the formulation that contains Agrol Diamond™ (formulation 4) has much higher biobased content than its counterpart without Agrol Diamond™: 66% vs. only 31%.

CONCLUSIONS

Agrol Diamond is a tri-functional natural oil-derived polyol of 86% biobased content. In addition to secondary hydroxyl groups, the polyol contains primary hydroxyl groups that dramatically increase its reactivity and ability to form rigid polyurethane networks. The BVT onset gelation time and the gelation time were consistently and significantly decreased with increased amounts of Agrol Diamond™ in Agrol® polyols. These results were observed with and without the presence of catalyst.

Table 2 Selected polyols completely miscible with Agrol Diamond™

Polyols Types	Examples
<u>Natural Oil Polyols</u> Soy polyols Castor oil Soy/PET polyols	Agrol® 2.0, Agrol® 3.0, Agrol® 3.6, Agrol® 4.3, Agrol® 5.6, Agrol® 7.0 Ecopol 115, Ecopol 122, Ecopol 123, Ecopol 124, Ecopol 131, and Ecopol 132
<u>Conventional Polyether Polyols</u> Poly(ethylene oxide) polyols Poly(propylene oxide) polyols Polyether polyols from varied starters	PEG 400, PEG 600 PPG 425, PPG 725, PPG 1000, PPG 2000 Pluracol P410R, Pluracol P2010, Pluracol 816, Pluracol 975, JEFFOL® SG-360, JEFFOL® SA-530, JEFFOL® SA-499, Arcol LHT-240, and VORANOL 370

Table 3 Effect of Agrol Diamond™ on increasing biobased content in water-blown polyurethane foam systems

Materials and Properties	1.6-pcf Open-cell foam (pour-in-place)		1.7-pcf Closed-cell foam (spray)	
	Formulation 1	Formulation 2	Formulation 3	Formulation 4
Agrol® 5.6 (parts*)	10		35	49
Agrol Diamond™ (parts*)		22		32
Biobased content ** (% in B-side)	40	50	31	66
Compressive strength (psi)	24	26	27	26

*Calculations are based on 100 parts of polyol components. **Calculated value

Agrol Diamond™ was found to be compatible with other commercially available natural oil polyols as well as conventional polyether polyols. It also showed complete miscibility with hydrocarbon blowing agents.

High reactivity and biobased content combined with excellent compatibility with other components make this polyol suitable for preparation of many biobased rigid polyurethane foams.

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BIOGRAPHIES



Ning Luo received a B.S. degree in Chemistry from Xiamen University, Fujian, China, and a Ph.D. degree in Polymer Materials Science and Engineering from the East China University of Science and Technology, Shanghai, China. He has worked in polymer materials for 25 years with different research institutions in China and in the United States. His research has contributed to diversified fields including rubber/plastics processing, copolymer synthesis, monomer synthesis, surface-functional materials, biomaterials, photopolymers, and polyurethane chemistry. Dr. Luo has served as the R&D Director for the BioBased Technologies[®], LLC since 2006. He currently focuses on the development of polyols and sustainable polyurethane materials from annually renewable resources. He has co-authored seventy-five peer-reviewed journal articles and four book chapters. He is also the co-inventor in six issued patents.



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