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BIO-BASED POLYOLS FOR THE FLEXIBLE SLABSTOCK FOAM INDUSTRY

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ABSTRACT

During the last few years, interest in polyols derived from natural oils has been constantly increasing for a variety of polyurethane applications. Bio-based polyol chemistry brings new product supply options that are produced from renewable resources, have supply stability and provide the opportunity for differentiation in the foam market-place. These are some of the key drivers for the polyurethane processors to look at ways to utilize such products. Until now, the successful use of natural oil-based polyols in flexible slabstock applications has been limited due to issues with quality consistency, odour, impact on physical properties and processing limitations. Most recently, Cargill Incorporated introduced its BiOH™ polyol product line for the production of flexible foams leveraging on the company's integrated supply chain and deep knowledge in processing oilseeds and vegetable oils on a global basis. Commercially available BiOH polyols are produced predominantly from soya-based feedstock. However, this article will show that Cargill can produce equally high quality polyols using palm feedstock. BiOH polyols are performance products produced with a chemistry that is completely detached from propylene or ethylene oxide. BiOH polyols have also resolved the odour and quality consistency issues previously encountered with other natural oil-based polyols. This article will describe the large-scale evaluation results of the first generation BiOH polyols in different foam grades and their ability to deliver the following: ease of processing with commercially available catalysts, surfactants and additives; improved flammability; improved hydrolysis resistance; performance enhancement in different foam grades such as viscoelastic; same level of microbial activity; more efficient load-bearing building capabilities than SAN copolymer polyols and smaller environmental footprint.

Keywords: palm, polyol, urethane, foam.

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INTRODUCTION

The consumer market has been going through a number of very significant changes over the last 10 to 15 years. More specifically, there appears to be a much greater sensitivity around issues like global warming, carbon footprint, pollution and the use of fossil fuels. The average consumer today is more than ever before likely to make decisions that reflect his or her bias towards protecting the environment. At times, these manifest themselves in terms of conserving energy and water use; on other occasions, when faced with an equal value decision, the customer will opt for the more responsible and environmental-friendly choice. More and more, we are seeing consumers willing to pay more for what is important to them – including the sustainability of the planet. Some years ago, such behaviour would have only been seen as relating to a small consumer niche. More recently this behaviour is moving mainstream.

As a consequence, we see a proliferation of 'green' products across a wide variety of markets. There is

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Note: BiOH™ is a registered trademark of Cargill Incorporated.

a range of options now available that leave a smaller environmental footprint – from products that are based on renewable materials to those that require less energy for production or use.

In the context of polyurethanes, a number of organizations have been trying for a long time to replace petro-polyols with more environmental-friendly analogs based on vegetable oils. More recently, such attempts have been primarily limited to rigid applications. The large flexible slab and molded applications have more or less been off-limits to bio-based polyols. Bio-based polyols could not find usage in such applications due to issues such as odour, lack of consistency and considerable loss in physical properties.

Cargill now offers the industry a large scale, reliable supply of bio-based polyols that actually perform in slab and molded applications. BiOH brand polyols perform month after month using our customers' existing foam equipment and traditional catalyst and surfactant packages. Not only has BiOH overcome the previous bio-based polyol issues like odour, but the products also impart certain physical property benefits, which will be discussed later in the article. Cargill has more than a century of experience in sourcing and processing agricultural raw materials. Now the company is using that experience to produce quality and value-added polyols for the foam industry.

A large number of flexible foam producers have been Cargill's regular customers for some time now, and are regularly using these polyols in a variety of foam products. BiOH polyols are today being shipped in tank truck and rail car quantities. This would not have been considered plausible only a few years ago, but now the future of BiOH polyols is here.

The foam industry has traditionally been dependent on petroleum and natural gas-based feedstock. More specifically, they are exposed to the supply and price volatility associated with propylene and propylene oxide. Now a polyol that is completely detached from propylene and propylene oxide is available to the industry.

Not only does that now present a more responsible choice to the industry, but it also diversifies their raw material sources. With diversification comes mitigation of risks around supply and price volatility – an option that the industry never had. By using BiOH polyols, the customers diversify their raw materials but do not have to compromise on quality.

Introducing a new and innovative product comes with its own challenges. It requires more than innovation on the part of the pioneers to commercialize the product and to create a new industry. Given that bio-based polyols constitute an emerging industry, it is appropriate to ask questions regarding its longevity. One of the key reasons for Cargill's success has to do with who we are as an organization. Cargill has been adding value to the things farmers grow for more than 140 years. Our high level of integration, starting from the grains that we buy from farmers to crushing, refining and polyol manufacture, is a key element in our ability to supply consistent and high quality products to the foam industry. There is not another bio-based polyol supplier that has a comparable scale and level of integration when it comes to agricultural processing.

STUDIES ON BIOH™ POLYOL

Foam Flammability and Physical Properties

Flexible slabstock foams were produced at 14 kg m^{-3}, 22 kg m^{-3} and 29 kg m^{-3} target densities in a continuous foaming process utilizing a production scale of the VARIMAX machine. Foam formulations were adjusted for the proper reactivity so as to attain similar air flows within each different grade. No adjustments in Toluene Diisocyanate Index (TDI) were done so that a better understanding of the effect of BiOH™ polyol on foam hardness and other physical properties could be obtained. The BiOH 5000 was introduced to the different foam grades up to 30 pph. Standard, commercially available catalysts, surfactants, flame retardant and other additives were utilized. The base polyether polyol utilized in combination with BiOH was a standard non-capped 3000 MW, triol with a 56 hydroxyl (OH) number. It was observed during foam production that due to their slower reactivity, the formulations processing latitude was increased when BiOH polyols were introduced. Formulations became less susceptible to variations in catalyst level, and the foamer had a higher degree of freedom to adjust the position of the blow-off line. Another interesting observation was that foams produced with BiOH polyols became more open as the amount of BiOH polyol was increased in the different foam formulations. This demanded an adjustment in the catalyst level so that foams with similar permeability could be produced for physical property comparison. It was also noticed that the density and initial 25% Indentation Load Deflection (ILD) gradients from top to bottom were lower for foams containing BiOH polyols. However, as validation of these claims would demand acquiring data over an extended period of time and across several seasons, these features will not be presented in this particular work and will be the subject of a more extensive evaluation.

Upon production, foams were cured for 24 hr after which samples were cut from the middle section of each block. Samples of 38 cm x 38 cm x 10 cm were taken from the top, centre and bottom sections of each block and conditioned for 48 hr at 25°C and 50% relative humidity prior to physical property testing. Foams were then tested according to the ASTM D3574 testing standard. Flammability was measured as per CAL 117 with the objective to look at burn lengths as a function of the different levels of BiOH polyol in each foam grade.

Table 1 shows a summary of foam physical properties and flammability behaviour as a function of foam density and level of BiOH polyol incorporation. It can be seen that there is an improvement in foam flammability directly proportional to the amount of BiOH polyol in the formulation as indicated by the shorter burn lengths.

The 25% ILD values were equivalent across the different levels of incorporation of BiOH polyol for the 14 kg m^{-3} and 22 kg m^{-3} foam grades. For the 29 kg m^{-3} foam grade, the effect of BiOH polyol on hardness was more pronounced. At this density grade, hardness can, however, be managed with adjustments in TDI index. Support factor, however, was improved as the BiOH polyol content increased.

Tensile strength, tear resistance and elongation values resulting from the addition of BiOH polyol were lower when compared to the controls, but still within the acceptable foam quality parameters for bedding and furniture applications.

Resilience and compression set values were equivalent and within the experimental error across the various foam densities and levels of incorporation of BiOH polyol.

Resistance to Moisture

Due to the high hydrocarbon content in vegetable oils, BiOH polyols are more hydrophobic than conventional polyethers. This feature can be translated into better resistance to moisture absorption in the final foams. This property is of particular importance across a number of applications such as garments, bedding (quilting) and specialty foams (squeegees and kitchen sponges). For these experiments, BiOH 5000 was compared with two polyether polyols as follows:

- polyether 1: A 3000 MW, 56 OH number, non-capped triol; and
- polyether 2: A 5700 MW, 31 OH number, capped, 3.8 functional.

The first experiment was set up to determine the moisture pick-up of these polyols individually over time. Each polyol of 10 g were weighed into a 75 ml aluminum dish of 3.81 cm (1.5 inch) diameter. The aged samples were placed in the Hotpack oven at 95°C and 95% relative humidity for 24 hr, 48 hr and 168 hr, while the control samples were stored under ambient conditions (25°C and 50% relative humidity). The samples were allowed to equilibrate to room temperature for 2 hr before the weighing and running water treatment using the Karl Fisher titration method.

Figure 1 shows the water absorption values for the three polyols over time at room temperature. The water pick-up rate for BiOH 5000 was significantly lower than for the comparative polyether polyols. *Figure 2* shows the same test but after heat-aged conditions. Even though there was an increase in the water absorption rate over time, the moisture pick-up rate of BiOH 5000 was still much lower than for the other two polyols.

The second experiment was set up to determine the moisture pick-up of the reacted polyols in cast elastomer films. This route was chosen for practicality and to eliminate any influence that the cell structure of foam may have in picking up water. Elastomers were prepared after the polyols were stripped of water and degassed at 80°C under vacuum with a roto-evaporator. The polyols were then mixed with a 98% p, p′ methylene diphenyl diisocyanate at a ratio of 1.02: 1.00 isocyanate/hydroxyl group (NCO/OH) in a dry glass beaker,

TABLE 1. FOAM PHYSICAL PROPERTIES AND FLAMMABILITY*

Density (kg m^{-3})	**14**			**22**			**29**			
BiOH (pph)	**0**	**10**	**20**	**0**	**10**	**20**	**0**	**10**	**20**	**30**
Air flow (cfm)	5.2	5.3	5.3	4.8	4.9	5.0	4.8	4.7	4.5	3.7
CAL 117 (cm)	5.5	4.6	4.3	4.9	4.6	3.0	5.2	3.9	3.6	3.3
25%ILD (lb 50 in^{-2})	22.6	22.7	22.2	32.1	31.8	31.3	24.6	21.8	23.5	22.5
Support factor	1.87	1.90	1.95	1.86	1.95	2.00	1.90	1.93	2.00	2.20
Tear (Nm^{-1})	368	298	263	438	263	315	333	245	193	175
Tensile (kPa)	92	82	81	98	71	93	83	85	67	65
Elongation (%)	182	158	162	212	180	157	207	147	149	153
Resilience (%)	39	36	37	41	38	36	53	46	44	39
90% comp. set (%)	21.3	21.1	20.1	11.8	11.9	12.6	4.4	5.4	7.2	9.1

Note: *CAL 117 – indicative values only. Not intended to represent foam behaviour under real fire conditions.

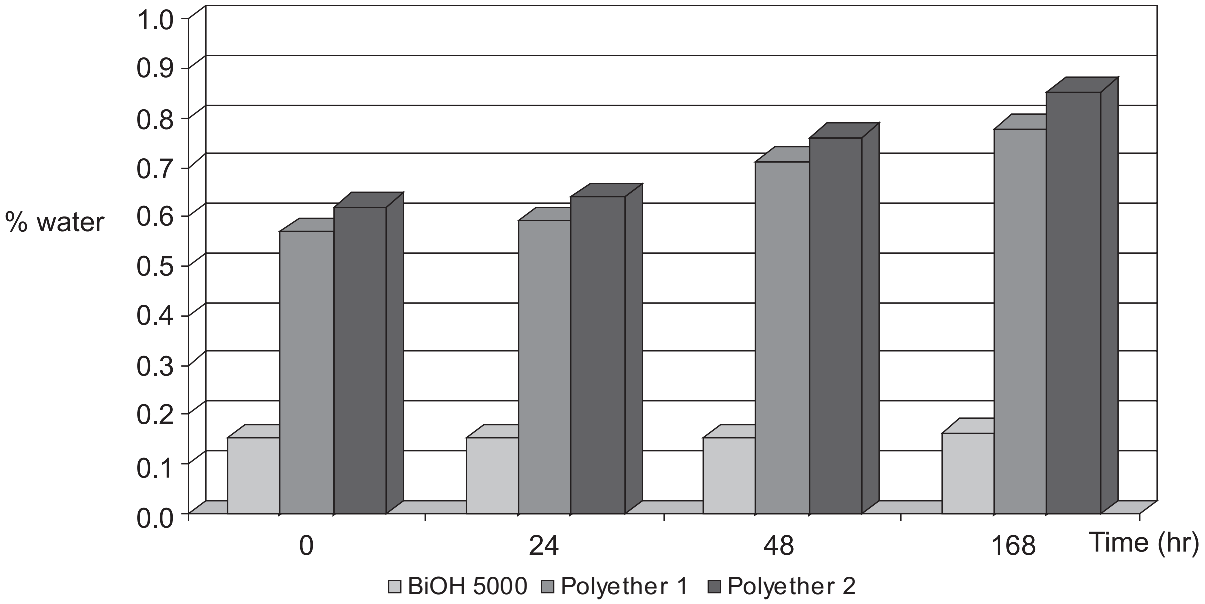

Figure 1. Water absorption (%) versus time (hr) for neat polyols at room temperature.

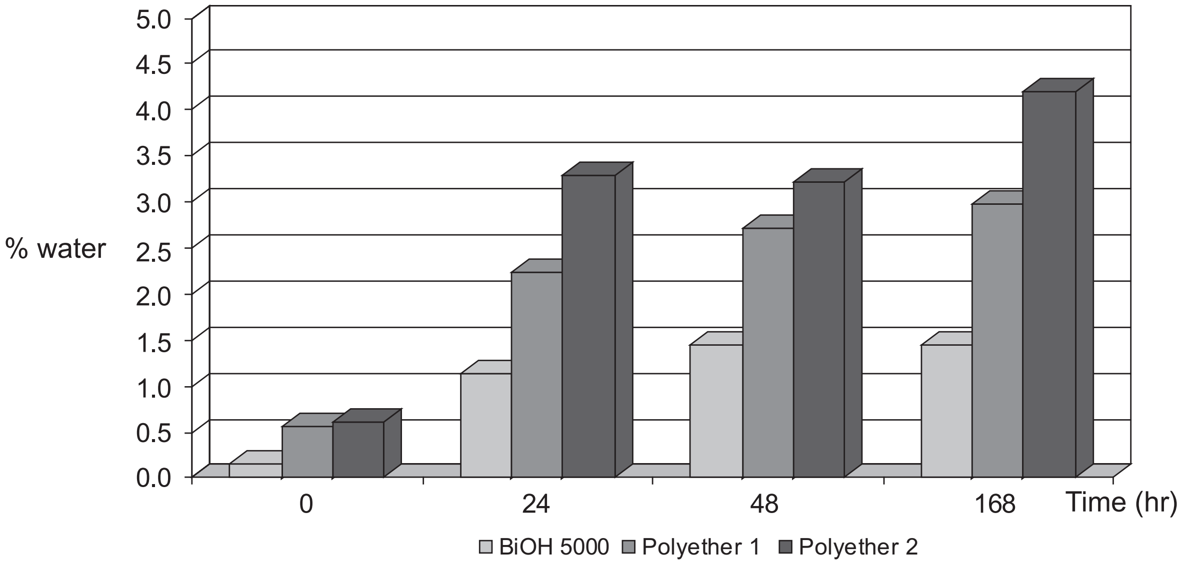

Figure 2. Water absorption (%) versus time (hr) for neat polyols after heat-ageing.

and then poured into a 10.16 x 10.16 cm (4 x 4 inch) mold. The mold was placed in an 110°C oven and allowed to cure for a minimum of 12 hr. Samples were then cut from the cast at ambient conditions for accelerated testing. Film thickness of the casts varied between 0.15 and 0.25 mm. Similar to the previous experiment, samples for accelerated testing were placed in the Hotpack oven at 95°C and 95% humidity for 24 hr, 48 hr and 168 hr.

Figure 3 shows the water absorption levels for the cast films at room temperature over time. As with the neat polyols, cast films prepared with BiOH 5000 showed remarkably better performance in terms of moisture pick-up when compared with the standard polyethers. The same behaviour was observed for the samples that were heat-aged as shown in *Figure 4*.

Microbial Activity

In order to determine their susceptibility to microbial and fungi activity, foams incorporated with BiOH 5000 were produced at different densities and different levels of incorporation as shown in *Table 2*. Foams were prepared in the laboratory by hand, targeting at the same airflows. Upon curing, foam samples were sent to an external laboratory (AppTec, Marietta, GA) for specified testing as given in *Table 2.*

Table 2 shows that, statistically, the population changes observed for each organism are of approximately the same order of magnitude for all the test samples, across all product compositions. The resulting data indicate that all compositions of

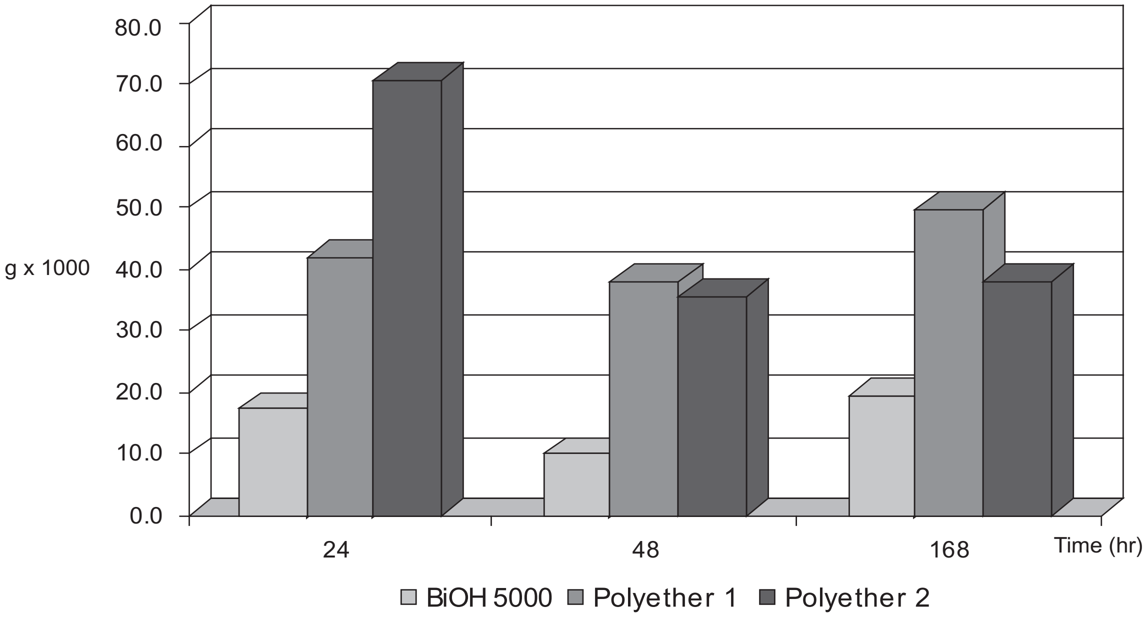

Figure 3. Weight gain (g) versus time (hr) for cast films at room temperature.

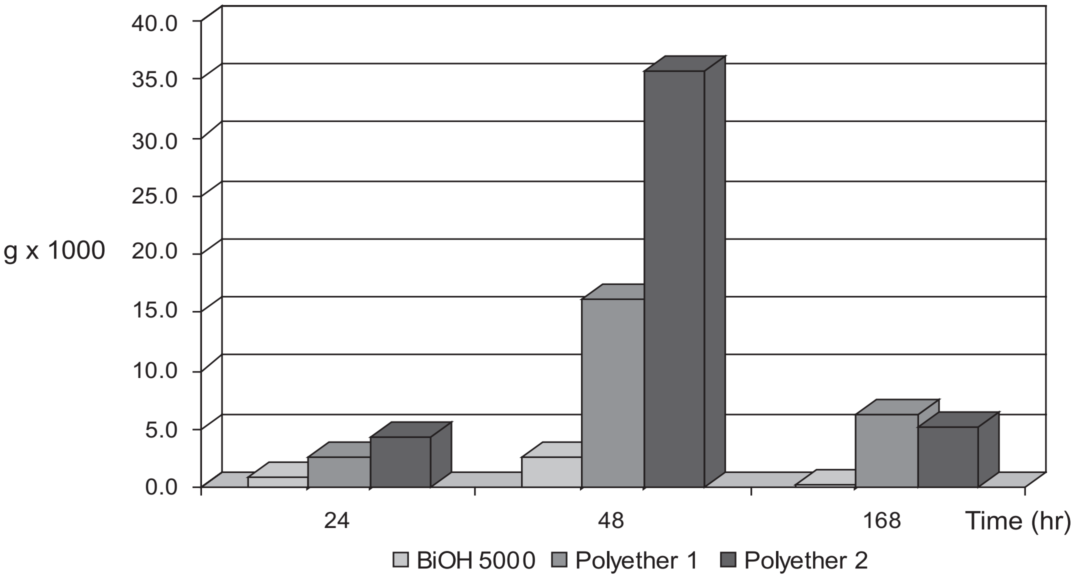

Figure 4. Weight gain (g) versus time (hr) for cast films after heat-ageing.

TABLE 2. MICROBIAL AND FUNGI ACTIVITY TESTS (average results)

Foam grade	**1.25**				**1.75**				**1.8**			
BiOH (pph)	**0**	**10**	**20**	**30**	**0**	**10**	**20**	**30**	**0**	**10**	**20**	**30**
Staphylococcus aureus ATCC6538 (x 10^6)	2.1	1.3	2.6	5.4	1.4	2.9	4.1	2.0	1.3	2.3	3.4	1.7
Klebsciella pneumoniae ATCC 4352 (x 10^7)	2.4	1.8	1.3	2.1	1.5	1.7	1.6	1.6	1.7	1.7	1.7	2.2
Aspergillus niger ATCC 16404 (x 10^4)	-2.5	-8.0	-4.0	-4.5	-2.0	-2.0	-7.0	-7.5	-8.5	-8.0	-5.0	-7.0

the polyurethane foam affect the growth pattern of each challenge organism in approximately the same manner.

Load-bearing Building in Molded Foams

BiOH polyols represent a new solid free option to build foam load bearing. BiOH 2100 was designed to replace styrene acrylonitrile (SAN) copolymer polyols commonly used for foam load bearing management. Although initially developed for flexible molded foams, work is in progress to facilitate its use in flexible slabstock foam formulations.

Figure 5 shows how BiOH 2100 at different levels of incorporation compares with a typical 43% solids SAN copolymer polyol in a 2.0 pcf T80 type toluene diisocyanate-based flexible molded foam.

Smaller Environment Footprint

A preliminary Life Cycle Analysis (LCA) indicated that the Cargill bio-based polyol process technology represents a significant opportunity for the reduction of primary energy demand of non-renewable fossil fuels, and a major reduction in emissions that contribute to global climate change, when compared to the petroleum-based polyol process technology. The total (renewable and non-renewable) primary energy demand of the Cargill polyol is 67.3 MJ kg^{-1} of product versus 87.9 MJ kg^{-1} of product for the petroleum-based polyol. This represents a 23% reduction in total primary energy demand. As the Cargill polyol energy demand is predominately renewable energy (mostly solar), demand reductions in non-renewable energy sources (oil, coal, natural gas, *etc.*) are even more pronounced. The Cargill process requires 61% less non-renewable primary energy to produce polyol than the petroleum-based polyol (33 MJ kg^{-1} of non-renewable for the production of Cargill polyol versus 85 MJ kg^{-1} of non-renewable for petroleum-based polyol). As a result of significant reductions in non-renewable fossil-based fuels, the potential impact associated with contribution to global climate change is greatly reduced as well. The production of the Cargill polyol results in 36% less emissions with global warming potential than the petroleum-based polyol. The results of the preliminary LCA indicated that Cargill's process to produce polyol reduces the reliance on fossil-based energy and feedstock, while cutting down on related greenhouse gas emissions when considered from a life cycle perspective.

USE OF PALM OIL IN CARGILL'S BIO-BASED POLYOLS

The commercially available BiOH polyols discussed above have been produced predominantly using soya-based feedstock. The reason for this is two-fold. First, soya is an abundant low-cost feedstock, and, second, soya is geographically close to the customers we currently serve. Cargill however is a global company and views the bio-based polyol trend in a global context. Thus, Cargill has done the experimental work to show that quality polyols can be made with a variety of vegetable oils including several grades of palm oil. Making flexible slabstock polyols from palm sources presented several challenges that have been resolved, including odour and phase stability at low temperature.

Physical and Chemical Properties of Palm Oil-based Polyols

A large series of laboratory experiments have been done showing that various palm oil grades

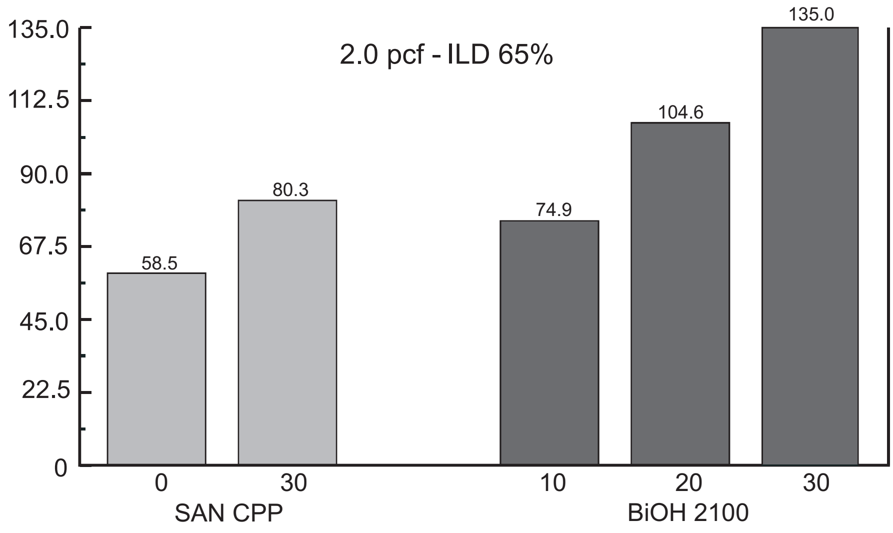

Figure 5. The BiOH 2100 load-bearing building ability.

(RBD palm, RBD palm olein, RBD palm super olein) can be hydroxylated to make polyols suitable for flexible foams. Cargill has demonstrated the ability to successfully control hydroxyl number and functionality over the range needed for flexible foams. *Table 3* shows the typical polyol properties of six experimental palm polyols compared to BiOH 5000.

Importantly, it was discovered that all the experimental palm-based polyols, except ExpPalm#6, had significantly lower viscosity than polyols prepared with soya at roughly the same molecular weight. This discovery has commercial importance, as customers will find that lower viscosity polyols are easier to pump into their storage tanks and to process in their foam machines.

Use of Palm Oil-based Polyols for Making Flexible Foams

Experiments have also shown that palm-based polyols can make flexible foams that are similar to those of the soya-based polyols. This conclusion was supported by laboratory foam data prepared with ExpPalm#1 and ExpPalm#2 mentioned above. In the preparation of the laboratory foams, the formulation in *Table 4* was used.

Laboratory foams were prepared by mixing all of the non-TDI components together in a 400 ml beaker at 19°C. The components were mixed by a laboratory mixer at 2340 rpm for 19 s. The TDI required by the above formulation was then added to the beaker and the whole system was mixed for an additional 6 s. The material was then poured into a 2.5 litre paper bucket and allowed to foam. To simulate the higher exotherms from large scale operations, the 2.5 litre paper bucket was cured in a 100°C ventilated oven for 15 min. The foam was then left to condition for no less than 72 hr at 25°C and 50% relative humidity. After conditioning, the foam was cut and tested according to standard industry methods. A detailed description of this methodology can be found in *Flexible Polyurethane Foams*, edited by Herrington & Hock, 2nd Edition, 1997, Dow Chemical Company.

The resulting foams produced by using this procedure with two experimental palm polyols were compared to the commercial BiOH 5000 polyol data presented earlier in the paper (*Table 5*). The comparison shows that palm-based polyols performed in a similar manner to the BiOH 5000 polyol based on soya. Palm-based polyols gave foams with density, hardness and airflow similar to the control. The extensive properties and resiliency were reduced somewhat with increasing palm polyol; while the compression set and support factor improved with increasing levels of experimental palm polyol.

It was found that flexible foams based on palm polyols achieved similar physical characteristics as foams based on soya polyols. Additionally, all experimental palm-based polyols in the article

TABLE 3. BIOH 5000 *vs.* EXPERIMENTAL PALM POLYOLS

Typical properties	**BiOH 5000**	**ExpPalm#1**	**ExpPalm#2**	**ExpPalm#3**	**ExpPalm#4**	**ExpPalm#5**	**ExpPalm#6**
Major vegetable oil	**Soya**	**Palm super olein**	**Palm super olein**	**Palm olein**	**Palm**	**Palm/soya**	**Palm olein**
Hydroxyl No. (mg KOH g^{-1})	56	41	51	44	62	70	53
Viscosity (Pa s@25°C)	4.5	0.66	0.94	1.15	1.18	3.1	7.3
Gardner colour	<1	<3	<3	3	<3	<3	<3
Molecular weight	1 900	1 406	1 474	1 944	1 976	1 773	1 677
Functionality (calculated)	1.9	1.03	1.34	1.5	2.18	2.21	1.60

TABLE 4. STANDARD EXPERIMENTAL FORMULATION FOR FLEXIBLE FOAM

Bio-based polyol	**X parts per hundred polyol (pph)**
Standard polyol – F3022	100-X pph
Water	3.98 pph
Surfactant EP-H-140	1.0 pph
Tin catalyst K20	0.22 pph
Amine catalyst B11	0.16 pph
TDI index	105

TABLE 5. FOAM PROPERTIES FOR BIOH 5000 *vs.* LABORATORY-SCALE PALM-BASED FOAMS

Bio-polyol	**BiOH5000**			**ExpPalm#1**			**ExpPalm#2**		
Foam Density (MJ kg^{-1})	**22**	**22**	**22**	**24**	**24**	**26**	**24**	**24**	**26**
BiOH (pph)	**0**	**10**	**20**	**0**	**20**	**30**	**0**	**26**	**30**
Air flow (cfm)	4.8	4.9	5.0	3.41	3.83	2.94	3.41	3.25	2.83
25%ILD (lb/50 in^2)	32.1	31.8	31.3	26.6	25.5	26.3	26.6	22.9	20.8
Support factor	1.86	1.95	2.00	1.73	1.96	1.92	1.73	1.93	2.18
Tear (N/M)	438	263	315	516	365	290	516	270	210
Tensile (kPa)	98	71	93	121	94	94	121	88	92
Elongation (%)	212	180	157	188	171	132	188	114	107
Resilience (%)	41	38	36	43	40	37	43	39	37
90% comp. set (%)	11.8	11.9	12.6	11.0	7.5	8.1	11.0	7.1	7.6

showed lower neat viscosities then BiOH 5000, which is an important advantage.

CONCLUSION

BiOH polyols represent a new low odour, quality consistent option in product supply that is separate from propylene. The first generation chemistry allows the incorporation of up to 30 pph of BiOH polyols to a wide range of flexible slabstock foam formulations using commercially available catalysts, surfactants and other additives. During foam production, formulations containing BiOH polyols show wider processing latitude and are less susceptible to changes in catalysts. Foams produced with BiOH polyols are, in general, more open as levels of incorporation increase, and show improvement in flammability, support factor, moisture resistance and improved load-bearing building capabilities. The production of BiOH polyols represents a smaller impact on the environment both from total energy consumption and global gaseous emissions standpoints. Finally, laboratory testing indicates that palm-based polyols can be made with lower viscosity than the soya-based polyols. These palm-based polyols can be made in a controlled process that allows them to achieve similar performance in flexible slabstock foams to those from soya-based polyols.

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