

Expanding the Use of Natural Oil Polyols in Urethane Foam Formulations

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Abstract

The desire to substitute the use of synthetic polyols, made from crude oil sources, with Natural Oil Polyols, from animal and vegetable sources, is always frustrated when insurmountable processing, or foam quality problems start to arise. This paper will present recent advances, which enable up to one hundred percent of the amount of the synthetic polyol in Urethane formulations to be replaced by Natural Oil Polyols of various kinds. New work, to develop novel, stable and foamable polymer dispersions based on a polyol containing at least 50% of a Natural Oil Polyol is also described.

Background

NOPs typically contain a large, wide distribution of different weight oligomers, which react at different rates as the main polyurethane polymerisation reaction proceeds. The molecular weight bell curve distribution for NOPs is therefore far flatter and lower than the tight, high bell curve of conventional (synthetic) polyols, which have been engineered and optimised over the years. Earlier research by Abraham et al (Reference 1) shows that low-level inclusion of NOP may be successful if 35% of oligomers are tetramers or higher, 5-10% are trimers and dimers are limited to 8-12 %. This scatter of polymers with different molecular weights leads to different NOP oligomers with different molecular weights reacting at different stages and times of the foam production reaction. An additional factor is that the hydroxyl groups on the NOP may be hindered from reacting with the isocyanate present in the foam formulation, because of the tangled oligomer structure of the base oil and therefore the NOP. These factors can create difficulties in processing, instability in slabstock and surface voiding in mouldings. This profusion of various short chain polymers present; typically leads to inferior physical properties in the finished polyurethane foam.

So, NOP levels need to be maximized **but**:

- ✓ Foam loses desired, familiar, physical properties and feel characteristics as NOP levels increase
- ✓ Foam becomes more unstable or has surface and internal faults (particularly in moulded foams) as NOP levels increase
- ✓ Reactivity of the system is greatly reduced; foam is softened.
- ✓ Persistent & distinctive NOP foam odour becomes stronger and longer lasting as NOP levels increase
- ✓ Maximum practical addition level of NOP to low density foams is less than 25 php

Mechanisms

Reactivity control

FATTY ACID COMPOSITION OF THE FOUR MOST ABUNDANT PLANT OILS (Reference 2)

Table 1

All Fatty acids	Soy	Palm Mesocarp	Rape High Erucic	Sunflower
14:0	-	0-15	-	-
16:0	8-13	22-46	3-4	5-7
16:1	-	0-2.5	-	<0.5
18:0	2-5	0.5-5	1-2	4-6
18:1	17-26	36-68	9-16	15-25
18:2(n-6)	50-62	2-20	11-16	62-70
18:3(n-3)	4-10	<1	7-12	-
20:0	<1	<0.5	-	<1
20:1	<0.4	-	7-13	<0.5
22:0	<0.5	-	-	<1
22:1	-	-	41-52	-

Each of the oils obtained from animal or vegetable sources contains a characteristic, but yet constantly changing range of saturated and unsaturated fatty acids. The molecular weight distribution of these fatty acids, for a given named oil, will therefore vary with the particular varietal that was planted but also with the soil type and weather pattern of the field that nurtured it. (Reference 3).

These effects are understood well in France in wine production and are called the effects of the "terroir".

Therefore, the raw material entering the NOP production process has a uniquely variable molecular weight distribution. Additionally, some of these fatty acid (oligomers) will also split, cleave, and even further add to the molecular weight scatter when subjected to the rigours of the NOP production process.

With so many variabilities in play, it would be hopeless for example to depend even on a genetically modified (say) soy bean grown under constant conditions and on the required large industrial scale, to produce a constant quality raw material for NOP production for use in urethanes. It would obviously be better to chemically "rectify" the raw material oil, or the final finished NOP to fit better into the Urethane foam process.

The technology invented by Green Urethanes (GU) preferentially reacts the short chain triglycerides of the NOP, especially monomers and dimer oligomers, into higher molecular weight polymers (Reference 4) using a combination of isocyanate and gelation catalysis. The most undesirable oligomers, and shortest chain molecules, will be preferentially reacted because they are naturally more reactive to the isocyanate and are preferentially "cleaned up". Additional chain extension reactions will then take place between other classes of oligomers leading to tri- and tetra- species, which will also then react with either lower or higher molecular weight oligomers or species. The various oligomers in the NOP in the order of their thermodynamic reactivity levels, are therefore reacted to form longer chain molecules. Arrhenius effects (kinetic effects) are minimised by carrying out this targeted reaction, preferably without the influence of heat.

These reactions, therefore, lead to a steeper and tighter bell curve distribution of oligomer species in the NOP. The forced formation of these macro molecules prior to and separate from the later foam production stage, leads to higher foam hardnesses, better processing and better physical properties compared to foams made with the inclusion of NOPs added without the "pre reaction" or "pre-treatment" stage, described here. It is possible and desirable to carry out this process on all of the polyol species present, in the same ratio mixture of NOP and synthetic polyol, which will be eventually used to make the final foam. A new homogeneous polyol is therefore created, which has singular and new characteristics, which are derived from the properties of the NOP(s) and synthetic polyol(s) used to form what is a new, hybrid, hydroxyl ended prepolymer.

This mechanism works over wide range and level of, NOP/ synthetic polyol mixtures and, isocyanates. These combinations create a new variety of cross-over hybrid polyols for use in the manufacture of flexible, semi-flexible and rigid foams. The foams have the features of improved flame retardancy and humid age properties - Humid age load loss - when compared to standard, non-hybrid, synthetic foams. These hybrid foams are also harder than standard synthetic foams.

From the foam production point of view, the foamer is now handed a completely new polyol, which acts and processes as a single, coherent material and not as a mixture containing two or more vastly different polyols with different reaction characteristics. These hybrids are storage stable.

Polymer dispersions

By choosing the architecture of the NOPs and synthetic polyols carefully, it is possible to form a new variety of GU Prepolymers, which will act as polyol component for a fresh series of stable Polymer Modified Polyols for example, based on the familiar PIPA, PHD or Acrylonitrile and Styrene technologies. These are useful in the manufacture of HR foam types.

Odour control

The characteristic odour given to foams as the percentage of NOPs is increased, has also been a problem for the furniture and bedding industries. These odourous materials, created during the NOP formation process, can be detected by more than 90% of humans at levels as low as 2 ppb; so attempts at their minimisation from about 30 ppm (Reference 1) down to these levels by physical means alone, even by a combination of high temperature and hard vacuum, has proved useless. By carefully choosing the correct combinations of isocyanate and catalysis forming the GU prepolymer, this characteristic odour is either eliminated or drastically reduced. The odour generating materials are not reacted out, but probably formed into a molecular complex, which wraps up these species and eliminates or minimises their annoyance to humans.

Results

GU Prepolymer formation and Odour control

Table 2: Changes in odour achieved with various catalysts in isocyanate-modified polyols

Typically, GU Prepolymers (isocyanate-modified polyols) are formed by reacting 100 parts of "polyol" with about 1 part of Isocyanate at ambient temperatures. The reaction is driven by a gelation catalyst, typically present at a level of 0.003 parts. The "polyol" may be an NOP alone, or any combination of NOP(s) and synthetic polyol materials. Table 2 shows a list of GU Prepolymers made to demonstrate the odour reduction properties of the Technology.

Component (pbw)	php								
	Ex 1	Ex 7	Ex 8	Ex 9	Ex 10	Ex 11	Ex 12	Ex 13	Ex 14
L4070	99	0	99	0	97	0	0	0	0
GreenB	0	99	0	99	0	100	99	99	99
M 220	1	0	0	1	0	0	0	0	0
Kosmos EF	0.003	0.003	0.003	0.003	0.003	0	0	0	0
Kosmos 54	0	0	0	0	0	0	0.003	0	0
DBTL	0	0	0	0	0	0	0	0.003	0
Sn Oct 33%	0	0	0	0	0	0	0	0	0.03
TDI	0	1	1	0	3	0	1	1	0.4
VDA Smell test									
Panellist 1	2	1	1 to 2	3	2	3	1 to 2	3	3
Panellist 2	2	1	2	3	2	3	2	3	3
Panellist 3	2	1	1	3	1	2 to 3	1	2 to 3	3
Panellist 4	2	1	1	3	1	3	1	3	3
Panellist 5	2	1	1	3	1	3	1	3	3

The BMW smell test (Table 2) was conducted according to protocol VDA 270/DIN 10955. This means that each odour panellist rates the odour according to the following scale:

1= No smell (Kein), 2= Slight smell, inoffensive (Nicht stoerend); 3=Easily detectable (Stoerend); 4=Uncomfortable smell (Unertraeglich); 5 = Very disturbing (Extrem). As illustrated in Example 11, NOP GreenB has an odour of 3. When this polyol is made into a modified isocyanate polyol as used in Examples 7,8,10 and 12 the odour level is reduced. The use of DBTL in combination with TDI in Example 13 does not reduce the odour nor does the use of stannous octoate in Example 14. Example 9 does not use TDI and does not reduce the odour when compared to GreenB alone (in Ex 11). Lupranol 4070 had an odour rating of 1 to 2 across all panellists. The key is therefore to preferably use TDI with metal salts of ricinoleic acid, as the gelation catalyst.

Source: Green Urethanes application

Reactivity control

Table 3 Comparison of flexible foam properties using various GU prepolymers

Pluracol 1388/4156	49						
Lupranol 4070		49			100		
GreenB Prepolymer	51	51					
GU (GreenB/P4156) 50/50 Prepolymer			100	100 Machine			
GreenB							
GU (GreenG/P4156) 50/50 Prepolymer						100	
GU (GreenH/P4156) 50/50 Prepolymer							100
Dabco 33LV	0.2	0.2	0.2		0.2	0.2	0.2
Amine A1	0,1	0,1	0,1		0.1	0.1	0.1
Stann. Oct 33%	0,7	0,7	0,7		0.7	0.75	0.7
Conventional Silicone	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Total Water	4	4	4	3.65	4	4	4
TDI php (Index 105)	52,2	52,2	52,2		50.1	52	52
Flame Retardant for Cal 117				12 -14			
Density PCF	1,4	1,46	1,5	1.8	1.6	1.5	1.52
Density kg/M3	22,4	23,36	24.0	29	25	24	24.3
CFD 40% kPa	4	2,95	3.7	3.2	4.1	3.49	4.09
ASTM IFD 25% Lbs	40	29,5	37	32	41	35	40
IFD after Humid age	31,2	23,9	27,8		27		28
Hardness loss %	22	18,9	24,8		34		30.5
Hysteresis	48,8	47,1	44		38	46	44
Tensile psi	12.6	13.2	14.9	11.8	16.8	13.3	17.5
Tensile kPa	87	91	103		116	92	121
Elongation %	126	160	182	148	189	152	160
Ball Rebound %					42	19	22
Comp Set @75%	14.3	15	8.5	7.5 @90%	7.3	8.2	8.5
SAG Factor (ILD)				2.38/2.4			

Laboratory data ó non optimised

Machine made - optimised

If the whole polyol element (NOP plus synthetic polyol) is subjected to this technology then the plasticising effect of the NOP during the foam production is minimised to the fullest possible level. The miscibility of the NOP element, the size of the macromolecule and optimisation of the physical properties, including the compression sets, of the material produced are further improved to the maximum extent. Note that standard foam chemicals are used at the foam preparation stages of all GU foams. Foams with levels of NOP at 50 php will typically be up to 25% harder than the equivalent synthetic product and need 25% less flame retardant to pass, say, Cal TB 117.

Stable Polymer dispersions

There are many new types of NOP worldwide, which are produced using a surprisingly wide range of technologies. Therefore, for example, there are at least three soy based polyols; but with primary hydroxyl percentages ranging from zero to one hundred percent. We have therefore looked at the NOP materials with relatively high primary content to see if they fit into the field of High Resilient foam technologies. This approach should work across PIPA, PHD and Acrylonitrile and Styrene dispersions. The new dispersions can be made either by forming the GU prepolymer as a first step, followed by making the dispersion in that GU prepolymer, or, forming the GU prepolymer and making the dispersion in it, as a single one-stage step. Below are some initial results from this exploration. The commencement of this work was originally announced at the recent Rome Europur meeting (Reference 5 & 6). However, here are the first figures, based on the PIPA process (Reference 7).

Table 4 High NOP Polymer Dispersions (HNPDS)

Laboratory Results	PHP	PHP
HNDPs	P14	P15
GreenH	50	50
V4701-5000 high EO polyol	50	50
Kosmos EF	0.003	
Bi Cat		0.03
Teoa 99%	4.7	4.7
TDI 80/20	5.4	5.4
Viscosity @25 mPas	5800	4600
Liquids Odour DIN 10955		
Panelist 1	1	1
Panelist 2	1	1
Foam preparation		
HNPD based PIPAs	100	100
Dabco 33LV		0.2
Amine A1	0.1	0.1
Deoa 90%	0.4	0.6
Stann Oct 33%	0.7	0.7
HR Silicone	0.1	0.1
Ortegol 204	0.8	0.6
Total water php	2.92	2.92
TDI php @ 105 Index	43.5	43.7
Density Kg/ m3	29.4	30.7
Density PCF	1.84	1.92
ASTM 25% ILD Lbs	44.5	43
CLD 40% (kPa)	4.45	4.3
CLD after Humid age	3.17	2.81
Humid Age Load Loss %	28.76	34.56
Tensile kPa	98	111
Tensile psi	14.2	16.1
Elongation %	125	125
Foams Odour DIN 10955		
Panelist 1	1	1
Panelist 2	1	1

As usual, all GU formulation work is on formulations where a minimum of 50% of the synthetic polyol is being replaced by 50 php of an NOP. This new family of foams respond to the normal rules of HR formulating, so that diethanolamine, Ortegol and HR silicone and water levels etc., may be varied over a wide range, in the normal manner, to open or close the foams and vary the density and hardness of the foam produced. The results worth commenting on are the relatively high level of the Tensile and Elongation figures. Normally HR does not have the very best results in this area, so these initial figures above, from foams containing 50 php of the NOP are remarkable. You will note that the PIPA formation appears to have removed the odour from the prepolymer and the final foams. These very satisfactory physical properties will further improve when the foams is produced, later this year, on a full scale foam machine. The formation of the HNPd can be done in one or more steps.

SAG factor Control

SAG Factor control of these HR foams and most foams containing over say 30 php of an NOP, is low, but, fortunately, GU has access to additional technology from a sister company Innochem, which can boost the ILD SAG factor of NOP foams to around 2.4 at the same time as enhancing the foam's Compression Sets. (Note: SAG Factors calculated from Compression Load Deflection measurements are generally a few percentage points lower than the IFD-calculated figure)

This Innochem technology is in routine use for production of a range of standard GU foams in the USA which contain 45 to 50 php of an NOP. The SAG factors can be enhanced to figures, which are typically between 2.38 to 2.44.

Conventional foams made with only synthetic polyols have ILD SAG factors of around 2.0 to 2.2, so this 2.4 level is already a great improvement. These GU conventional foams may therefore be classed as High Comfort types.

The work on HNPds, mentioned above, is very new, and we have not yet applied the Innochem technology to these formulations. However we are confident that it will enhance the two particularly important properties of SAG Factor and Compression Set, in the expected manner.

75 and 100 php Foams

Table 5

GU 100 php Prepolymer (GreenJ)			100
GU 75/ 25 php Prepolymer (GreenH + synthetic polyol)		100 Machine	
GU 75/ 25 php Prepolymer (GreenK + synthetic polyol)	100		
Conventional Silicone	1	1	1
Dabco 33LV	0.2	0.2	0.2
Amine A1	0.1	0.1	0.1
Water	4	4	4
Stannous Octoate 33%	0.7	0.4	0.4
TDI Index	105	105	105
		M	
Density kg/ m3	23.7	24.5	24.2
Density PCF	1.48	1.53	1.51
CLD 40% kPa	3.39	4.65	3.93
ASTM ILD 25% Lbs	34	46	39
Tensile psi	4.9	6.7	5.6
Tensile kPa	45	62	88
Elongation %	125	123	124
Humid Age Load Loss %	33	NA	26.2

Laboratory and **M**achine Results

These are results with two different, development NOPs (GreenJ & K) made in laboratory pilot plant apparatus, which are not yet in production. The middle foam listed is from commercially available GreenH and is not fully optimised, but is machine made. Note the hardness increase when using GreenH.

Both bench made foams (from J & K) processed normally and the physical properties are good and will improve even further when they are run on a full scale foam machine.

Foams made with 75 php of NOP should have a Certified Green content of about 50% by weight; foams at 100 php will have Certified Green contents around 73% by weight. These foams have not been certified at Beta Analytic Inc.

Conclusions

It is now possible to replace the synthetic polyol element in flexible Urethane foams and satisfy the accepted physical property criteria. This GU technology has been in routine operation in the North American market for the past 24 months. About 15 grades of foam all with NOP levels at 50 php have been sold into the furniture and bedding markets there, at densities typically running between 20 and 30 kg/m³ – 1.25 to 1.875 pcf. Foam hardnesses are controllable over a wide range, at these densities, of about 14 to 50 ASTM 25% pounds, being 1.4 to 5.0 CLD kPa. Additionally, via Innochem technology, the foams are made with SAG Factors normally associated with those of High

Comfort foams. These foams have none of the shortcomings of processing or “dry feel” of foams, which have had even relatively small levels of NOP added to them.

Green Urethanes has opened the door to a new range of High NOP Polymer Dispersions (HNPDs) which will find use particularly in HR and high load bearing foams.

Successful basic formulation work has already been done on a variety of soy, palm and rapeseed oil based, NOPs. Our next task is to start to look at the various combinations of different NOPs in conventional foams, which will further widen the extent of this very interesting technology.

We have also started application of this field to Rigid foams technology. We think the new hybrid nature of the GU prepolymers may solve the sluggish reaction and lower flame retardancy normally experienced by laminators when incorporating NOPs into their rigid foam grades.

Experimental laboratory test materials used

The following materials were used;

GreenB – soy oil based all secondary OH polyol, BioH 5000, Cargill Inc., USA,
GreenG – palm mesocarp all secondary OH polyol, F 6037, Polygreen Chemicals, Malaysia
GreenH - soy oil based 50% primary OH polyol, Merginol 207, Hobum GmbH, Germany,
Development GreenJ – new technology laboratory NOP from undisclosed source J
Development GreenK – new technology laboratory NOP from undisclosed source K
Lupranol 4070 – trifunctional polyol with glycerol starter, PO backbone and tip, BASF AG
Pluracol 1388 (aka Pluracol 4156 – (DMC)) Hetero polyol - 56 OH triol, from BASF Inc. USA
Voranol 4701 – high EO High primary 5000 mol wt triol , The Dow Chemical Company, USA
Voramate M220 - polymeric MDI , The Dow Chemical Company, USA
Kosmos EF – catalyst of tin ricinoleate, Evonik AG, Germany
Kosmos 54 – catalyst of zinc ricinoleate, Evonik AG, Germany
Bi Cat – Bismuth based gelation catalyst, Shepherd Chemical Company, Ohio, USA
Stann Oct/Sn Oct 33% - Stannous Octoate 33% solution (ubiquitous)
Deoa 90% - solution of Diethanolamine in water (ubiquitous)
DBTL –Dibutyl tin dilaurate- Sigma Aldrich Co.UK
Ortegel 204 – cross linker , Evonik AG, Germany

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Biography



Jeff Rowlands

Jeff Rowlands is a Director of Green Urethanes Limited and also, its sister company Innochem Limited. Both companies are involved in the development, patenting and licensing of in house, and third party-developed, technologies, for use in the Urethane foam industry, worldwide. Both GU and Innochem are based in the United Kingdom. Prior to this, he was a Director of Interchem International SA in Luxembourg, which developed and licensed the PIPA polyol process for use in the North American and European flexible slabstock and moulding markets. He was also Technical Director of Beaverfoam Manufacturing (now part of Recticel NV) in the UK. His first job after university in Manchester UK, was as a Unit production engineer and later, troubleshooter at Union Carbide's chemical facility in Southern England. Jeff is a Fellow of the Institution of Chemical Engineers, a Chartered Engineer and a registered European Engineer at FAENI in Paris.