

The Adjustment of Physical Properties of Viscoelastic Foam – the Role of Different Raw Materials

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ABSTRACT

Viscoelastic polyurethane foam, also referred to as memory foam or low resilience foam, is used mainly in home and office furnishings, although a considerable amount of work has been conducted for automotive applications. During a compression cycle, viscoelastic foams exhibit slow recovery and thus, high hysteresis. Viscoelastic foams also typically have low ball rebound values. They are produced from MDI, TDI 65, TDI 80 and other mixtures of these isocyanates. TDI 80 formulations have a tendency toward closed cell structures, whereas TDI 65 and MDI usually result in foams with reasonable porosity. The role of the cell structure – cell fineness and porosity – turns out to be significant for viscoelastic foams relying on the pneumatic as well as the adhesion effect. The major reason for viscoelastic foam properties however is the glass transition temperature, which is mainly defined by the nature of the polyol mixture. By the specific adjustment of the glass transition temperature, also other foam physical properties (such as foam hardness or compression set) are controllable.

Evonik has put many resources into the understanding of the different mechanisms, which influence the physical properties of viscoelastic foam. This paper evaluates different ways to control and precisely adjust physical properties of viscoelastic foam. Finally, the influence of different raw materials on the viscoelasticity and other physical properties of the foam are analyzed.

INTRODUCTION

Viscoelastic polyurethane foam, also referred to as memory foam or low resilience foam, finds an increasing interest in PU industry [1, 2]. It is mainly used in home and office furnishings, although a considerable amount of work has been conducted for automotive applications. The main application is in the high quality mattress segment, where the viscoelastic foam distributes the body weight over a larger area [3]. In addition, vibration damping and sound absorption are other applications, but to a lower extent. During a compression cycle, viscoelastic foams exhibit slow recovery and thus, high hysteresis. Viscoelastic foams also typically have low ball rebound values. They are produced from MDI, TDI 65, TDI 80 and other mixtures of these isocyanates. While the production of TDI 65 or MDI viscoelastic foam is less problematic, viscoelastic formulations based on TDI 80 have a tendency toward closed cell structures, which often result in shrinkage.

In order to understand why the cell structure is of such exceptional importance for the properties and the viscoelastic behavior of viscoelastic foam, it is necessary to understand the effects, which are responsible for the viscoelasticity of the foam (Figure 1). Polyurethanes are polymers containing a three dimensional network originated from the addition polymerization of the raw materials, namely the polyols and the polyisocyanates. When compressing such a network it produces a resilient force. In order to achieve the typical slow recovery after deformation it is necessary to compensate this resilient force by reversed effects. For that purpose, three other effects, which counteract the network effect, have to be maximized, namely the pneumatic effect, the adhesive effect and the relaxation effect.

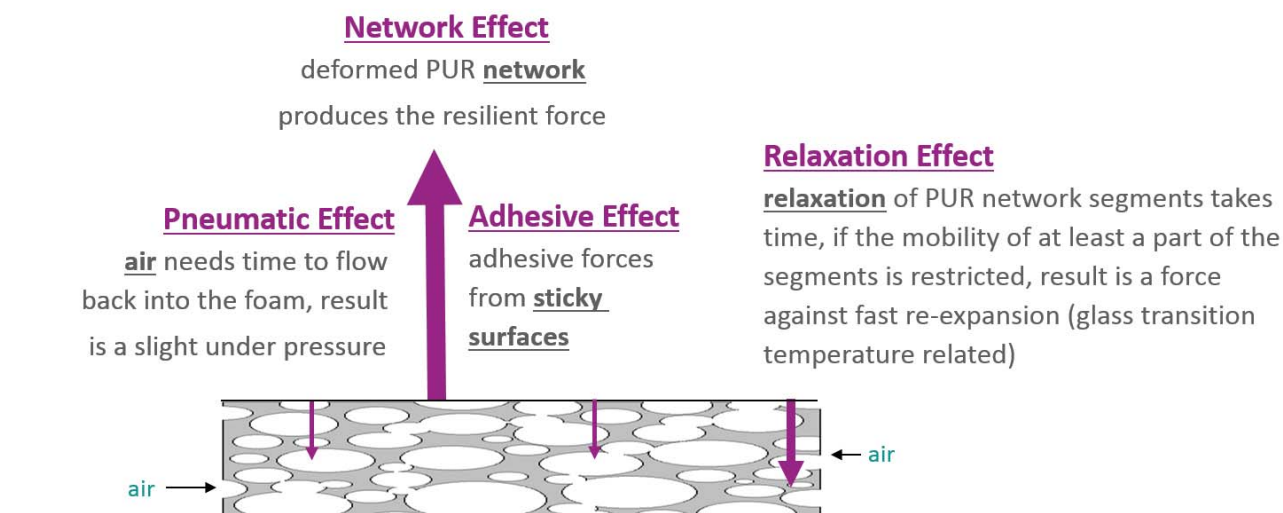


Figure 1. Schematic drawing of the different forces involved in the behavior of viscoelastic polyurethane foams.

The relaxation effect

The major reason for viscoelastic foam properties is the unusual high glass transition temperature (T_g), which is typically slightly below or roughly at room temperature. The glass transition is defined as the temperature range where the polymer goes over from a hard and glassy state to a soft and rubbery material. Unlike melting temperature, which is a thermodynamic property of solid material, T_g is a dynamic property for amorphous polymers and it is related to relaxation behavior of local chain segments. As a result, T_g depends on the following factors affecting the mobility of chain segments: cross-link density in the network structure, aromaticity (weight fraction of aromatic structures in the polymer matrix), plasticizer concentration, and so on [4, 5]. Due to its dynamic attribute, for a given polymer, T_g can adopt a range of values identified using various characterization techniques such as dilatometry, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). In this work, DSC was used to locate T_g . Details about the different characterizing method and their interpretation can be found elsewhere [6, 7]. Figure 2 shows representative DSC graphs of a viscoelastic PU foam (exo down). The blue curve indicates changes in heat flow during the first heating cycle of the foam whereas the green curve shows the variations of enthalpy during cooling. When a polymer is stored at its glass temperature an endothermic relaxation peak can occur when the sample is heated for the first time. This peak however is obtained neither when the sample is cooled nor when it is heated up again shortly after cooling. Therefore, in order to minimize errors due to such relaxation peaks for evaluation of the DSC graphs in this study the second heating curve was used (see red curve in figure 2).

The mechanical properties of such viscoelastic flexible foams do depend on the ambient temperature. Elevated temperatures (above usual ambient conditions) reduce the viscoelastic behavior making the foam feel more like soft conventional foam. On the other hand, lower temperatures cause the viscoelastic foam to turn quite hard and too viscoelastic (no or extremely slow recovery from deformation).

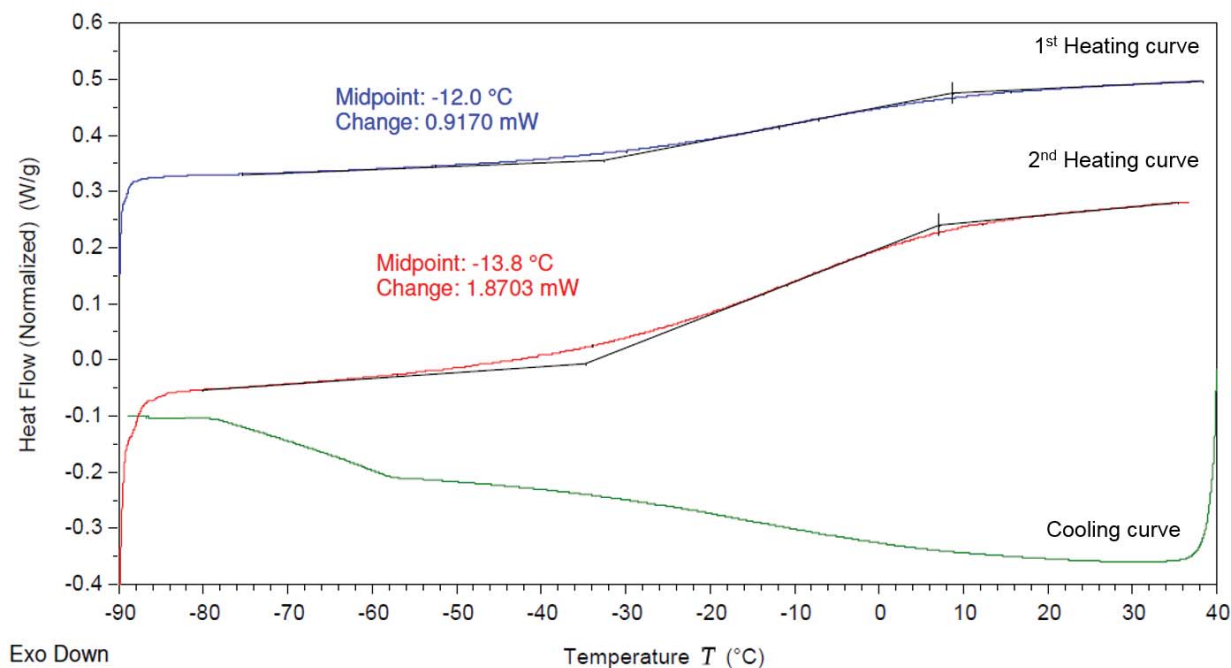


Figure 2. Representative DSC graphs of a viscoelastic PU foam.

The glass transition temperature of conventional ether foam is far below ambient temperature. The reason can be found when having a closer look at the molecular structure of a conventional compared to a viscoelastic foam (Figure 3). Polyurethane foams are complex mixtures of polyols, isocyanates, and other modifiers that are combined to form an intricate network of hard and soft domains. A typical viscoelastic foam formulation contains several types of polyols. The main part usually comprises one or more so-called visco- or cross-linker polyol. A quite high OH number (commonly between 150 and 250 mg KOH/g) and thus a low molecular weight (usually 700 – 1000 g/mol) characterize this kind of polyol. Using such polyols raises the density of network nodes, results in the presence of shorter chain segments from one network point to the next and shifts the glass transition temperature in the direction of higher values. Owing to the high glass transition temperature of viscoelastic foams, some network segments are still frozen, and restricted in their mobility, at room temperature. This affects the resilience of the entire polyurethane network and elicits a time-retarded behavior. The glass transition takes place across a temperature range and is not limited to a specific temperature because the length of the network segments follows a certain distribution.

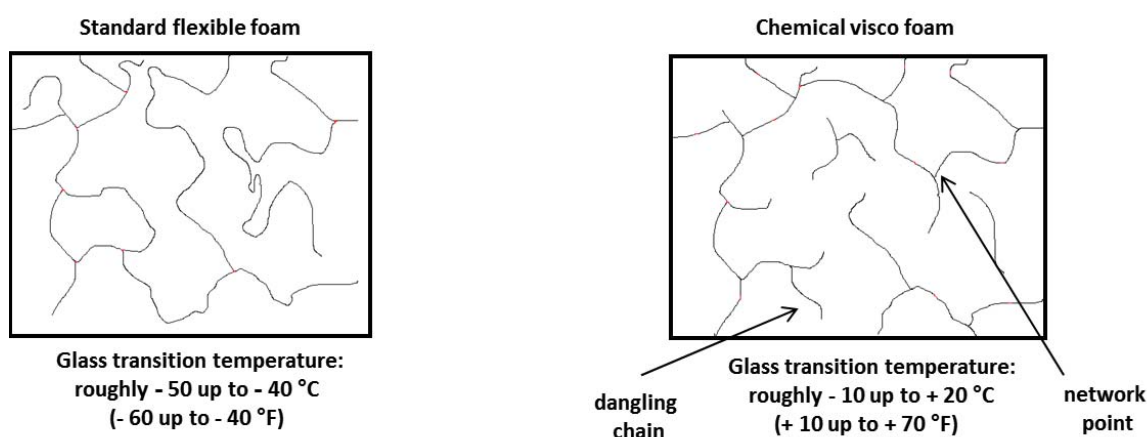


Figure 3. Schematic drawing of the molecular level of a conventional and a viscoelastic foam showing the reason for different glass transition temperatures.

In order to soften the foam usually a second kind of polyol is used which is characterized by a relatively low OH number (Hypersoft polyol, OH# about 25 – 35 mg KOH/g). Additionally viscoelastic foam generally is produced at low index which leads to an incomplete curing and thus to a high number of dangling chains which also make the foam softer. Foam producers usually also use a certain quantity of conventional polyol to obtain acceptable mechanical properties. Details are apparent from the literature [1, 2, 8]. Viscoelastic foams that are dependent on the relaxation effect and according to that whose slow relaxation after deformation is defined by the nature of the polyol are called chemical visco foams.

The adhesive effect

A second reason for the viscoelastic properties is also related to the glass transition temperature. Polymers, which are handled closely to their glass transition temperature, are sticky materials. All attractive and adhesive forces between struts and membranes cause this stickiness when foam is compressed and foam structure elements get in touch. Results from previous published experiments [4] show that this tackiness is dependent on the internal surface of the foam and thus on the cell size. The recovery time of the viscoelastic foam is increased when the number of cells is increased and so the cell size is decreased. Viscoelastic properties become very strong when the foam is very fine and possesses a big internal surface (Figure 4).

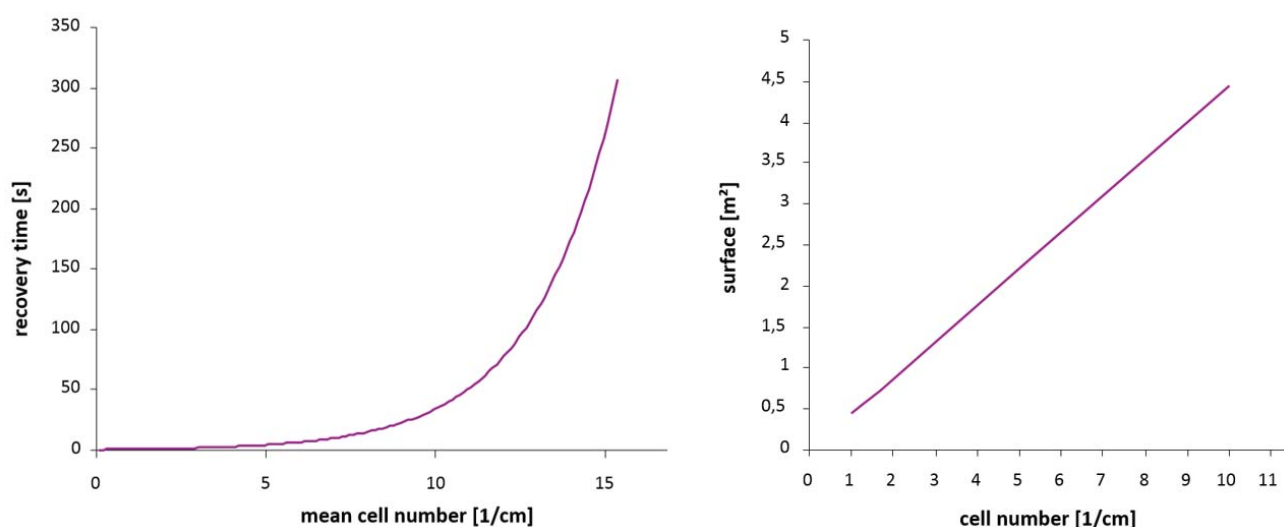


Figure 4. Dependency of the recovery time of a viscoelastic foam on the cell number and the internal surface.

The adhesion between foam structure elements may have several reasons. Mechanical entanglements of struts may be one aspect, liquid surface films a second, hydrogen bridges and van-der-Waals bonds a third. Molecular entanglements of the polymeric network segments may also be a factor as well as reactive linkages, although unlikely. Whatever the reason, the key is that membranes stick together and delay the re-expansion. As the adhesive effect is not only a matter of the glass transition temperature but also of the cell structure, it is both a molecular as well as a macroscopic effect.

The pneumatic effect

The third effect counteracting the resilient force and being responsible for the viscoelastic properties is dependent on the porosity of the foam. When a foam with a tight cell structure is compressed, the foam needs time to take up air again. The nearly closed cells make the foam slow and a slight underpressure results, which acts against the fast re-expansion. The pneumatic effect is thus a macroscopic effect and dependent on the cell structure.

The goal in achieving the desired viscoelastic properties of the polyurethane foam is to balance the resilient force from the network with the three opposite effects. The important aspects of the different forces are summarized in Table 1.

Table 1. Characterization of the different forces involved in the viscoelastic behavior of polyurethane viscoelastic foams.

	Molecular or Macroscopic	Applies to both Compression and Re-Expansion	Temperature Influence	Cell structure Influence
Network Resilience Effect	Molecular	yes	Yes, weak	Yes, weak
Relaxation Effect	Molecular	yes	yes	no
Adhesion Effect	both	no	yes	Yes, strong
Pneumatic Effect	Macroscopic	yes	no	Yes, strong

Typically, slabstock viscoelastic foams rely more on the relaxation effect. The adhesive effect is especially important for fine celled viscoelastic slabstock foams while molded viscoelastic foams are often more focused on the pneumatic effect. Typical viscoelastic foams exhibit all three effects to some extent, but the contribution of the different effects varies. Therefore, for nearly all viscoelastic foams, the precise control of the glass transition temperature is required in order to obtain the desired viscoelasticity and mechanical properties. The role of cell structure turns out to be significant for all viscoelastic foams based on the pneumatic and adhesive effect and therefore a careful control of cell regulation and cell opening is essential for the production of viscoelastic foam.

OBJECTIVE

Viscoelastic properties of chemical visco foams are varied by shifting the glass transition temperature. Minimal changes in the glass transition temperature also have a direct influence on the mechanical properties such as hardness or resilience of the foam formed. Modulating the manufacturing formulations of viscoelastic foams to match the climate characteristics of the particular market is accordingly very important. Foam mattress buyers would sometimes like the feel or firmness of the mattress in the store, but found it too hard or soft in their house, depending on the home temperature. This issue set new glass transition requirements and created trends to vary the T_g and for foams to be less temperature sensitive. This work evaluates different ways in order to control and precisely adjust physical properties of viscoelastic foam and to determine the influence of different raw materials on the viscoelasticity and other physical properties of the foam. The paper presents an investigation of the glass transition temperature as a function of cross-link density, aromaticity, and plasticizer concentration, for several water-blown PU model systems. The value of T_g reflects the rigidity of polymer matrix, which influences mechanical strength, dimensional stability, long-term aging behavior, and other properties. Therefore, understanding the relationship between structure and T_g can considerably accelerate the development of new systems.

EXPERIMENTAL

Foams produced for this study were made by hand pouring in the laboratory. In order to evaluate different physical properties of viscoelastic foams, Evonik has developed two TDI based visco formulations resulting in foams with different densities (table 2). The final foam density of formulation 1 is 45 kg/m³ (2.8 pcf) and formulation 2 is density of 50 kg/m³ (3.1 pcf).

All foams were made using 250 g of polyol with the other constituents of the formulation scaled accordingly. Here, for example, 1.0 part of a component means 1 g of this substance per 100 g of polyol. For all formulations the polyols, amines, water, stannous octoate and other additives were added into a paper cup and stirred for 60 s at 1000 rpm using a disc stirrer. The isocyanate was then added and the mixture again stirred 7 s at 1500 rpm using the same stirrer. The whole mixture was poured into an insulated foaming box with a size of 20 x 20 cm and 25 cm in height. The box was wrapped with a non-adhesive paper inside. The insulation of 5 cm standard ether foam was required to prevent the foam from rapid cooling. Foams were allowed to cure for 24 hours and cut afterwards. The following measurements were taken and recorded: rise time, height, settling after 3 min, air permeability of the foam, CLD hardness at 40% compression after 24 hours, cell size, and ball rebound. OH-numbers were determined according to Ph. Eur. 2.5.3 Method A and expressed as *mg KOH/g*.

Mechanical analysis has been done by using a Zwick 1445 Test Machine. Resiliency was determined by the ball rebound test. Rise measurement was made by using Dr. Wehrhahn Ultrasonic Foam Rise Detection equipment. Cell structure analysis has been made by a flatbed scanner and image analysis software (a4i from Soft Imaging Systems). Porosity measurements were made by using the backpressure method. A constant air stream of 100 l/h is forced to flow through a 5 cm thick sheet of the foam, cut perpendicular to the rise direction. The resulting backpressure is measured in mm water column. High values indicate a very tight cell structure. The range is from 1 mm water column (very open) to > 300 mm water column (very closed). Reference foams are marked in bold letters.

DSC measurements have been done by using the differential scanning calorimeter Discovery DSC from TA Instruments equipped with the TA Instruments Trios V3.2 software. Samples were placed in standard aluminum pans (item no. 900794.901), equilibrated at -90 °C and finally subjected to the following temperature program:

1	Equilibrate -90.00 °C	
2	Isothermal 2.00 min	
3	Ramp 10.00 °C/min to 40.00 °C	(1 st heating curve)
4	Isothermal 2.00 min	
5	Ramp 10.00 °C/min to -90.00 °C	(cooling)
6	Isothermal 2.00 min	
7	Ramp 20.00 °C/min to 40.00 °C	(2 nd heating curve)
8	Isothermal 2.00 min	

Glass transition temperatures were determined using the second heating curve and are expressed in °C.

<i>Table 2. Basic formulations for viscoelastic slabstock foams. The amounts of raw materials and additives are given in parts per hundred parts (pphp).</i>		
	Formulation 1	Formulation 2
Density	45 kg/m ³ (2.8 pcf)	50 kg/m ³ (3.1 pcf)
Cross-linker polyol 1 (OHN 228)	70	
Cross-linker polyol 2 (OHN 185)		92
Conventional polyol (OHN 48)	30	
Hypersoft polyol (OHN 34)	12	8
TDI T80	40.3	41.8
Index	85	93
Water	1.95	1.7
Evonik ORTEGOL 204		1.6
Evonik TEGOAMIN [®] 33	0.3	0.3
Evonik TEGOAMIN [®] BDE	0.2	0.15
Evonik TEGOAMIN [®] DMEA	0.2	
Evonik KOSMOS [®] 29	0.07	0.03
Evonik Cell Opener ORTEGOL [®] VCO	variable	variable
Evonik Silicon Surfactant	variable	variable

RESULTS AND DISCUSSION

The customary way to modify the glass transition temperature is either to vary the cross-link density of the polyurethane network, or to vary the chemical composition of network segments. The former is easily done in the case of flexible polyurethane foams by varying the ratio of isocyanate groups to isocyanate-consuming groups (the “index”). It is further possible to take advantage of the functionality of various multifunctional compounds to shift the glass transition temperature by adding these compounds. Cross-linking components (functionality > 2) raise the glass transition temperature, while components having a functionality < 2 lower the cross-link density. Chemical modifications to network structures relate to the chain length of the polyols and monomers used. These modifications all require relatively large changes to be made to the formulations, changing many other parameters besides the glass transition temperature (e.g. rise times in foaming, air permeability, settling or cell structure). This means that making such changes to the cross-link density becomes a complex undertaking.

Shifting the glass transition temperature – Variation of the cross-link density

Variation of the index

For this series of experiments, foams based on formulation 2 were prepared using the same combination of silicon surfactant and cell opening additive with indices increasing from 82 to 98. We used 0.5 parts TEGOSTAB[®] BF 2470 as foam stabilizer and 1.0 parts of ORTEGOL[®] VCO as cell opening additive. Table 3 and Figure 5 depict the effect of the ratio of isocyanate

groups to isocyanate-consuming groups on the glass transition temperature and other physical properties of the resulting visco foams.

Entry		1	2	3	4	5	6	7
Index		82	84	87	90	93	96	98
TEGOSTAB® BF 2470	[pphp]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ORTEGOL® VCO	[pphp]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Rise time	[s]	130	126	125	125	120	120	120
Porosity	[mm]	18	29	57	60	80	111	120
Cells	[cm ⁻¹]	10	10	11	11	11	10	10
CLD 40% (24 h)	[kPa]	0.8	1.1	1.3	1.8	2.3	2.7	3.1
Ball rebound	[%]	6	6	6	6	6	6	6
Glass transition temperature (T _g)	[°F]	-10.7	-5.3	-3.1	0.9	7.3	11.7	14.0
Glass transition temperature (T _g)	[°C]	-23.7	-20.7	-19.5	-17.3	-13.7	-11.3	-10.0

The increase in index moved T_g to higher temperatures. This is a reasonable outcome as the cross-linking is increased and thus the density of network points augmented. The mean length of the chain segments from one network point to the next is shortened and so there is more energy needed to mobilize these segments. With an index of 82 a glass transition temperature of -23.7 °C and accordingly -10.7 °F was observed (entry 1, table 3) whereas with an index of 90 T_g increased to -17 °C (1 °F, entry 4, table 3) and with an index of 98 it increased to -10 °C and 14 °F, respectively (entry 7, table 3). However with an increasing index also other physical properties shifted: CLD 40% hardness is increased from 0.8 kPa (index 82) to 3.1 kPa (index 98) whereas airflow is decreased from 18 mm H₂O (entry 1) to 120 mm water column (entry 7). Overall, in this formulation it was possible to increase T_g by 0.9 °C (1.6 °F) per index point.

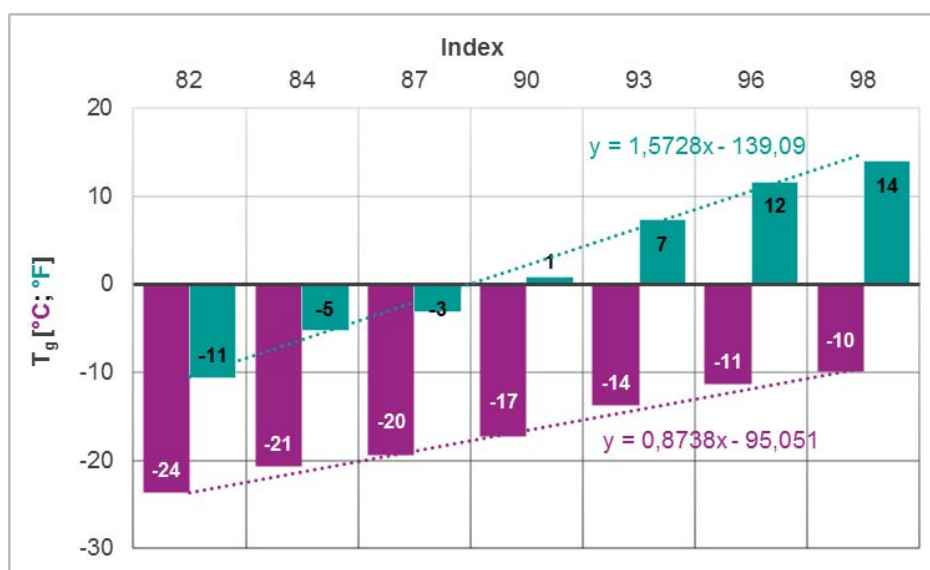


Figure 5. Glass transition temperature of foams based on formulation 2 as a function of index.

The effect of cross-linkers and chain extenders

Cross-linkers are generally used in order to prevent splits, strengthen the chemical network and harden the polyurethane foam. Hence, they should also be able to influence the glass transition temperature of a visco foam. We chose ORTEGOL® G as a cross-linker and ORTEGOL® CXT as a chain extender in order to investigate the impact on T_g and other physical properties of foams being produced according to formulation 2 (table 4 and figure 6).

Table 4. Physical properties of foams based on formulation 2 using cross-linkers or chain extenders.

Entry		8	9	10	11	12	13	14	15
ORTEGOL® G (OHN 1350)	[pphp]		0.2	0.6	1.0				
ORTEGOL® CXT (OHN 1244)	[pphp]					0.5	1.0	1.5	2.5
TEGOSTAB® BF 2470	[pphp]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ORTEGOL® VCO	[pphp]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Rise time	[s]	120	145	140	140	185	146	140	126
Porosity	[mm]	80	81	95	142	85	87	95	113
Cells	[cm ⁻¹]	11	10	10	11	11	11	11	11
CLD 40% (24 h)	[kPa]	2.3	2.5	2.7	3.2	2.6	2.7	2.8	2.9
Ball rebound	[%]	6	6	7	6	6	6	6	6
Glass transition temperature (T _g)	[°F]	7.3	8.2	9.5	12.9	9.5	10.8	12.7	16.2
Glass transition temperature (T _g)	[°C]	-13.7	-13.2	-12.5	-10.6	-12.5	-11.8	-10.7	-8.8

An increasing amount of ORTEGOL® G as well as of ORTEGOL® CXT led to a raise in T_g. With 1 part of ORTEGOL® G the glass transition temperature increased from -13.7 °C (7.3 °F, reference, 0 pphp ORTEGOL® G, entry 8, table 4) to -10.6 °C (12.9 °F, 1 pphp ORTEGOL® G, entry 11, table 4). In the course of this, hardness also rose from 2.3 kPa to 3.2 kPa whereas airflow was lowered from 80 to 142 mm backpressure. When we used 1 part of ORTEGOL® CXT, we only observed a little increase in hardness from 2.3 kPa to 2.7 kPa and a minor increase in airflow (entries 8 vs. 13, table 4). However the glass temperature raised by nearly 2 °C or 3.5 °F accordingly (from -13.7 °C, 7.3 °F to -11.8 °C, 10.8 °F). Even when applying 2.5 parts of ORTEGOL® CXT the resulting foam was still sufficiently open (113 mm H₂O, entry 15, table 4) and T_g could be increased to -8.8 °C, 16.2 °F respectively. On average, the glass temperature raised by 0.3 °C (0.5 °F) with an increase of ORTEGOL® G by 0.1 parts and by 0.2 °C (0.4 °F) per 0.1 parts of ORTEGOL® CXT.

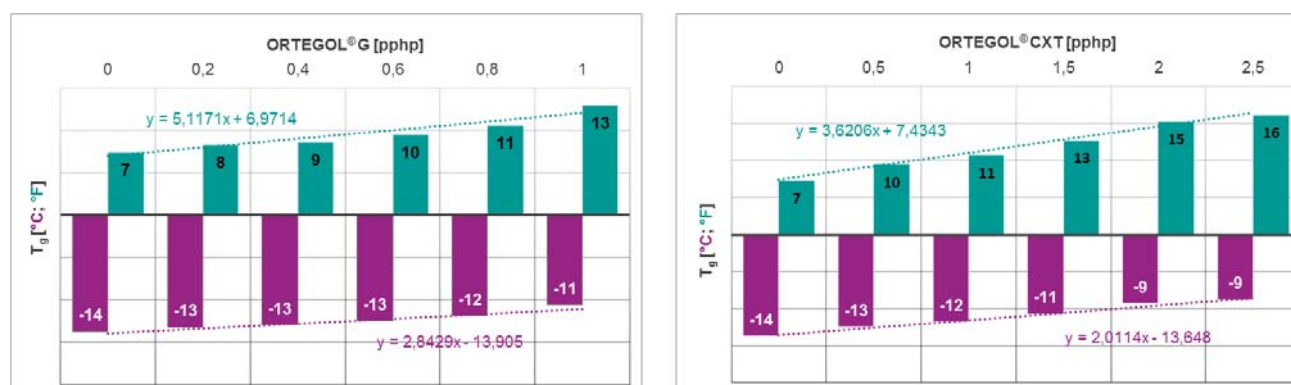


Figure 6. Glass transition temperature of foams based on formulation 2 when using ORTEGOL® G as a cross-linking agent (a) or ORTEGOL® CXT as a chain extender (b).

We also investigated the influence of ORTEGOL® 204 on the glass temperature of foams based on formulation 2. ORTEGOL® 204 is a cross-linking agent with a delayed reaction, specially designed for the production of high resilience and viscoelastic polyurethane slabstock foams. Although ORTEGOL® 204 should increase the density of network points we did not notice a significant change in the glass transition temperature. Hardness and cell number however increased with rising amount of ORTEGOL® 204 while porosity virtually stayed constant. The results are summarized in table 5.

Table 5. Physical properties of foams based on formulation 2 with variation of the amount of ORTEGOL 204.

Entry		16	17	18	19	20	21	22
ORTEGOL® 204 (25% H ₂ O, OHN 880) [pphp]		0	0.5	1	1.6	2.0	2.5	3.0
TEGOSTAB® BF 2470	[pphp]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ORTEGOL® VCO	[pphp]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Rise time	[s]	137	115	110	120	143	130	120
Porosity	[mm]	77	78	71	80	83	81	71
Cells	[cm ⁻¹]	7	9	9	11	11	11	12
CLD 40% (24 h)	[kPa]	1.6	1.8	1.9	2.3	2.3	2.6	2.8
Ball rebound	[%]	6	6	6	6	7	7	6
Glass transition temperature (T _g)	[°F]	5.4	2.7	5.5	7.3	6.1	10.2	3.9
Glass transition temperature (T _g)	[°C]	-14.8	-14.3	-14.5	-13.7	-14.4	-13.1	-14.6

Monofunctional alcohols as softening agents

Monofunctional alcohols are commonly used to soften viscoelastic foams. They act as a chain-breaking agent and build so called dangling chains (see above, figure 3). In theory, they lower the cross-link density and thus the glass transition temperature should decrease when increasing the load of monofunctional softening agents. When we used ORTEGOL® 315 as a softening agent in formulation 2 it was possible to prove this theory. The outcomes are summarized in table 6 and illustrated in figure 7. By applying 0.5 parts of ORTEGOL® 315 the T_g is decreased by 1.6 °C or 2.8 °F accordingly (T_g = -15.3 °C, 4.5 °F, entry 26, table 6) compared to the reference foam (T_g = -13.7 °C, 7.3 °F, entry 23, table 6). A higher loading of 1 part of ORTEGOL® 315 resulted in an even lower glass temperature (-16.7 °C, 1.9 °F, entry 27, table 6).

Table 6. Physical properties of foams based on formulation 2 using monofunctional softening agents.

Entry		23	24	25	26	27
Benzyl alcohol (OHN 518)	[pphp]		2.5	5.0		
ORTEGOL® 315 (OHN 54)	[pphp]				0.5	1.0
TEGOSTAB® BF 2470	[pphp]	0.5	0.5	0.5	0.5	0.5
ORTEGOL® VCO	[pphp]	1.0	1.0	1.0	1.0	1.0
Rise time	[s]	120	180	180	157	170
Porosity	[mm]	80	28	17	14	6
Cells	[cm ⁻¹]	11	10	8	9	8
CLD 40% (24 h)	[kPa]	2.3	1.6	0.9	2.0	1.6
Ball rebound	[%]	6	6	6	6	6
Glass transition temperature (T _g)	[°F]	7.3	14.9	17.4	4.5	1.9
Glass transition temperature (T _g)	[°C]	-13.7	-9.5	-8.1	-15.3	-16.7

However when using benzyl alcohol as a chain breaking agent we observed the opposite behavior. Although the hardness of the resulting foams was reduced by the softening agent we noticed an increase of the glass temperature: With 2.5 parts of benzyl alcohol a T_g of -9.5 °C, 14.9 °F respectively (entry 24, table 6), was obtained and with 5 parts we observed a T_g of -8.1 °C and 17.4 °F accordingly (entry 25, table 6). On average T_g raised by 1.1 °C (2.0 °F) per 1 part of benzyl alcohol. Lifeng Wu et al. discussed the impact of the aromaticity on the glass transition temperature of rigid polyurethane foams [5]. According to their study, a higher content of aromatic substructures in the system results in an increased T_g. This might be an explanation why benzyl alcohol raises the glass temperature while a non-aromatic monofunctional softening agent (ORTEGOL® 315) decreases the T_g.

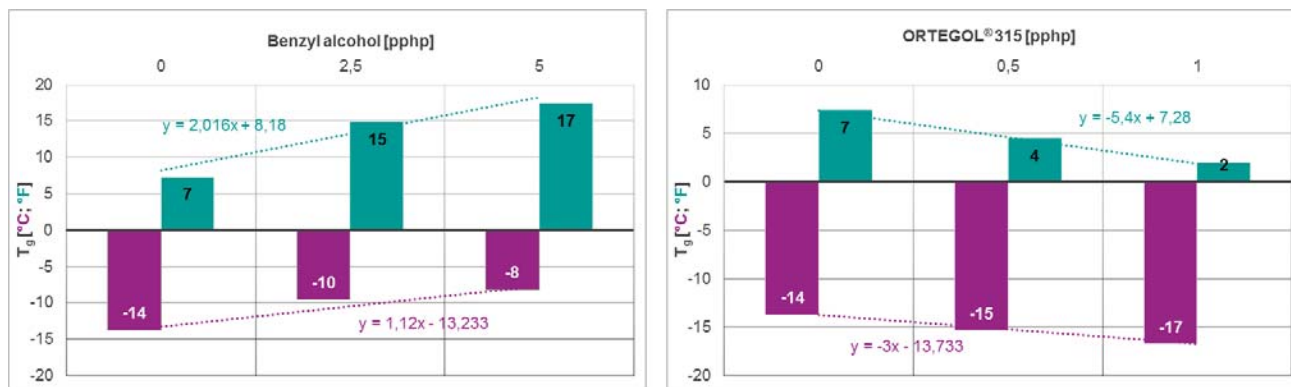


Figure 7. Glass transition temperature of foams based on formulation 2 when using monofunctional alcohols as softening agents.

The effect of plasticizers

Plasticizers also influence the physical properties of viscoelastic foam and therefore should have a certain impact on the glass transition temperature. They swell the network structure and dilute the aromaticity of the system and therefore a decrease in T_g is expected [5]. In this study ORTEGOL® 310 (softening agent for conventional flexible foam) and TCPP (tris-(2-chloro-1-methylethyl) phosphate) were chosen as plasticizers and used in different use levels in formulation 2 (table 7 and figure 8). TCPP was chosen because it has been widely used as flame retardant in conventional flexible foam. In both cases indeed, a decrease of the T_g was observed when the amount of plasticizer was increased. When we applied 0.8 parts of ORTEGOL® 310 the glass temperature decreased by 2.9 °C or 5.2 °F accordingly ($T_g = -16.6$ °C, 2.1 °F, entry 30, table 7) compared to the reference ($T_g = -13.7$ °C, 7.3 °F, entry 28, table 7). However, increasing the amount of ORTEGOL® 310 decreased the airflow of the resulting foam and with 1.2 parts of ORTEGOL® 310, we eventually observed a shrinkage. TCPP – a little bit less effective than ORTEGOL® 310, but with a broader processing latitude – decreased T_g by an average of 0.6 °C (1.0 °F) per part of the flame retardant. When we used 3 parts of TCPP, we obtained a foam with a glass transition temperature of -16.6 °C (2.1 °F, entry 32, table 7). By increasing the load of TCPP the T_g could further be decreased to -17.7 °C, 0.1 °F respectively (entry 34, table 7).

Table 7. Physical properties of foams based on formulation 2 using different plasticizers.

Entry		28	29	30	31	32	33	34
ORTEGOL® 310	[pphp]		0.4	0.8	1.2			
TCPP	[pphp]					3.0	5.0	7.0
TEGOSTAB® BF 2470	[pphp]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ORTEGOL® VCO	[pphp]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Rise time	[s]	120	121	126	shrinkage	123	124	120
Porosity	[mm]	80	110	162	-	70	65	73
Cells	[cm ⁻¹]	11	10	12	-	11	11	10
CLD 40% (24 h)	[kPa]	2.3	2	1.9	-	2.1	2.0	1.8
Ball rebound	[%]	6	7	7	-	5	5	6
Glass transition temperature (T _g)	[°F]	7.3	5.9	2.1	-	2.1	1.4	0.1
Glass transition temperature (T _g)	[°C]	-13.7	-14.5	-16.6	-	-16.6	-17.0	-17.7

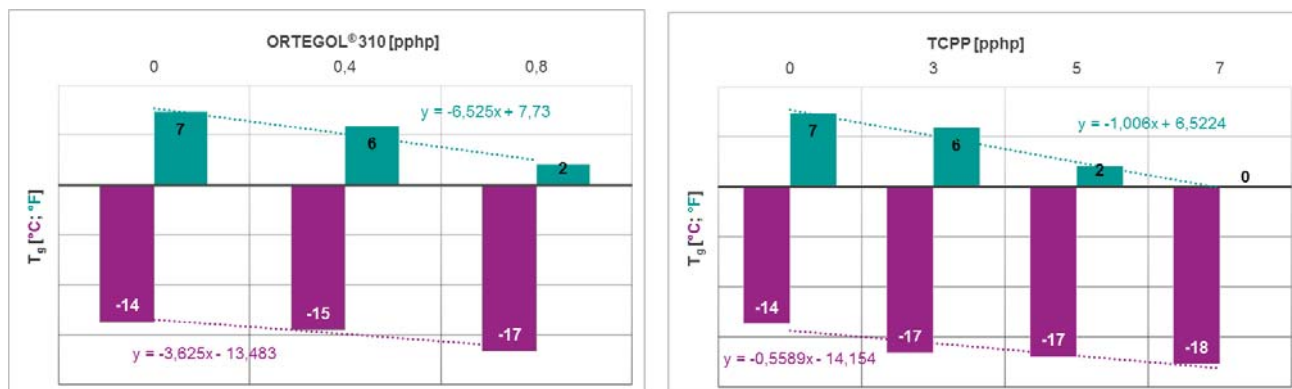


Figure 8. Glass transition temperature of foams based on formulation 2 when using ORTEGOL® 310 (a) or TCPP (b) as plasticizers.

Variation of the catalysis

In order to investigate the influence of the catalysis on the viscoelastic properties several foams based on formulation 2 were prepared by varying the amount of TEGOAMIN® 33 and KOSMOS® 29. Again, the same combination of silicon surfactant and cell opening additive was used as before. The amine catalyst was gradually increased and simultaneously the amount of tin catalyst was decreased little by little. The results are displayed in table 8 and figure 9.

Table 8. Physical properties of foams based on formulation 2 with variation of the tin and amine catalyst.

Entry		35	36	37	38	39	40	41
TEGOAMIN® 33	[pphp]	0.3	0.33	0.39	0.45	0.51	0.57	0.6
KOSMOS® 29	[pphp]	0.03	0.027	0.021	0.015	0.009	0.003	0
TEGOSTAB® BF 2470	[pphp]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ORTEGOL® VCO	[pphp]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Rise time	[s]	120	126	128	135	120	118	115
Porosity	[mm]	80	67	60	61	61	74	75
Cells	[cm ⁻¹]	11	10	9	9	9	11	11
CLD 40% (24 h)	[kPa]	2.3	2.2	2.2	2.3	2.2	2.4	2.3
Ball rebound	[%]	6	7	7	6	5	7	6
Glass transition temperature (T _g)	[°F]	7.3	4.3	3.0	1.4	-0.9	-2.9	-5.3
Glass transition temperature (T _g)	[°C]	-13.7	-15.4	-16.1	-17.0	-18.3	-19.4	-20.7

While hardness and porosity nearly stayed constant, the glass transition temperature shifted to lower temperatures when decreasing the amount of KOSMOS® 29 and increasing the load of TEGOAMIN® 33. The reference foam with 0.3 parts of TEGOAMIN® 33 and 0.03 parts of KOSMOS® 29 (entry 35, table 8, bold figures) showed a T_g of -13.7 °C and accordingly 7.3 °F. Decreasing the load of tin catalyst to 0.015 parts and increasing the amine to 0.45 resulted in a T_g of -17.0 °C and 1.4 °F, respectively (entry 38, table 8). When we completely removed the tin catalyst and used 0.6 parts of amine, we obtained an even lower glass temperature -20.7 °C and -5.3 °F (entry 41, table 8). Due to the constancy of other physical properties, this might be a useful tool for the production and use of viscoelastic mattresses in rather cold areas of the world or in wintertime.

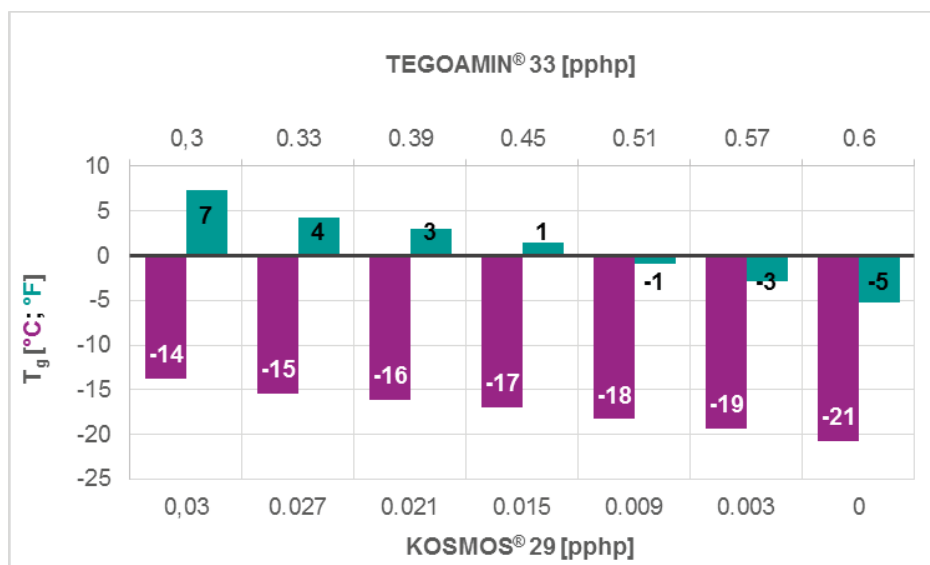


Figure 9. Variation of the glass transition temperature of foams based on formulation 2 with variation of the catalysis.

Shifting the glass transition temperature – Chemical modification of network structures

As already mentioned above it is possible to shift the glass transition temperature by chemically modifying the network structures of the visco foam. As the T_g is mainly dependent on the chain length of the polyols, in a first series of experiments, we changed the mean OH number of the polyol blend of formulation 1 and thus the mean chain length. For this purpose we gradually replaced the basic visco polyol with OH number of 228 mg KOH/g by an experimental visco polyol (functionality $f = 3$) with an OH number of 196 mg KOH/g. Thus, the mean OH number of the polyol blend was reduced from 157.8 mg KOH/g (entry 42, table 9) to 139 mg KOH/g (entry 46, table 9). Reducing the mean OH number means increasing the mean length of the network segments from one network point to the next and therefore a lower T_g would be expected. As shown in table 9 and figure 10a, a decrease of the glass transition temperature was observed from $-26.4\text{ }^\circ\text{C}$ ($-15.5\text{ }^\circ\text{F}$, entry 42, table 9) to $-32.9\text{ }^\circ\text{C}$ ($-27.2\text{ }^\circ\text{F}$, entry 46, table 9). The reduction of the mean OH number is also attended by an increase in airflow. With a mean OH number of 157.8 mg KOH/g, a low airflow is obtained (300 mm H₂O) whereas with an OH number of 139 mg KOH/g a very open visco foam is generated (15 mm backpressure).

Table 9. Physical properties of foams based on formulation 1 with variation of the mean OH number of the polyol blend (variation of polyol structure I).

Entry		42	43	44	45	46
Cross-linker polyol 1 (OHN 228)	[pphp]	70	50	30	15	0
Cross-linker polyol 1b (f = 3, OHN 196)	[pphp]	0	20	40	55	70
Conventional polyol (OHN 48)	[pphp]	30	30	30	30	30
Hypersoft polyol (OHN 34)	[pphp]	12	12	12	12	12
TEGOSTAB® BF 2470	[pphp]	0.5	0.5	0.5	0.5	0.5
ORTEGOL® VCO	[pphp]	2.0	2.0	2.0	2.0	2.0
Mean OH number of polyol blend	[mg KOH/g]	157.8	152.4	147.0	143.0	139.0
Rise time	[s]	180	180	180	180	180
Porosity	[mm]	300	300	160	40	15
Cells	[cm ⁻¹]	15	15	15	15	15
Glass transition temperature (T _g)	[°F]	-15.5	-16.2	-19.3	-24.3	-27.2
Glass transition temperature (T _g)	[°C]	-26.4	-26.8	-28.5	-31.3	-32.9

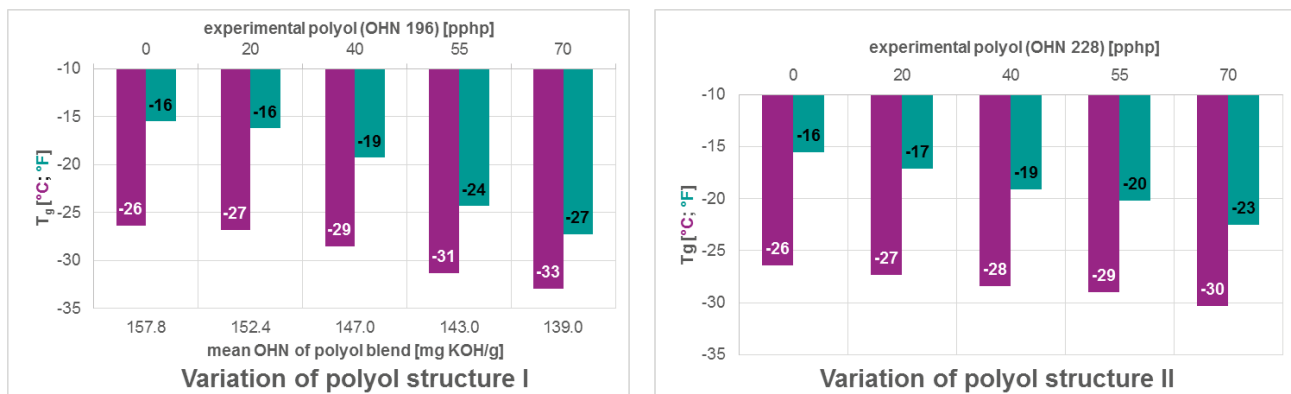


Figure 10. Variation of the glass transition temperature by changing the mean OH number of the polyol blend (a) and by changing the cross-linker polyol structure (b).

In a second series of experiments, we replaced the basic cross-linker polyol in formulation 1 by a second experimental cross-linker polyol (functionality $f = 3$) with different chemical structure. The OH number and therefore the molecular weight of this polyol is virtually identical to the basic polyol. Therefore, the mean OH number of the polyol blend was not changed and a shift of the glass transition temperature was not expected. Actually, T_g was reduced when we increased the ratio of the experimental polyol. The outcomes are summarized in table 10 and figure 10b. An entire replacement of the fundamental cross-linker polyol by the experimental polyol resulted in a T_g that was 4 °C (7 °F) below the T_g of the reference foam (reference: -26.4 °C, -15.5 °F, entry 47, table 10 compared to -30.3 °C, -22.5 °F, entry 51, table 10). Using this new experimental polyol also seems to be beneficial in terms of airflow. While obtaining a very fine cell structure in all cases a higher ratio of experimental polyol leads to more open foam structures (entries 47 – 51, table 10). This is a very interesting outcome as cell opening of TDI viscoelastic foams always is a critical issue.

Table 10. Physical properties of foams based on formulation 1 with variation of the chemical structure of the polyol blend (variation of polyol structure II).

Entry		47	48	49	50	51
Cross-linker polyol 1 (OHN 228)	[pphp]	70	50	30	15	0
Cross-linker polyol 1c ($f = 3$, OHN 228)	[pphp]	0	20	40	55	70
Conventional polyol (OHN 48)	[pphp]	30	30	30	30	30
Hypersoft polyol (OHN 34)	[pphp]	12	12	12	12	12
TEGOSTAB® BF 2470	[pphp]	0.5	0.5	0.5	0.5	0.5
ORTEGOL® VCO	[pphp]	2.0	2.0	2.0	2.0	2.0
Rise time	[s]	180	180	180	180	180
Porosity	[mm]	300	300	177	135	80
Cells	[cm ⁻¹]	15	15	15	15	15
Glass transition temperature (T_g)	[°F]	-15.5	-17.1	-19.1	-20.2	-22.5
Glass transition temperature (T_g)	[°C]	-26.4	-27.3	-28.4	-29.0	-30.3

SUMMARY

Since the glass transition temperature of viscoelastic polyurethane foams is just below room temperature, the viscoelastic as well as the mechanical properties are strongly influenced by the ambient air temperature. For a given glass temperature of a foam a few degrees variation in the surrounding temperature will have a strong impact on the feel or firmness of a mattress. That is why a user friendly and precise control of the glass transition temperature is required in order to match the climate characteristics of particular markets for viscoelastic polyurethane foam.

In this study, several ways to increase as well as to decrease the glass transition temperature of viscoelastic foams and impacts on physical properties were discussed. The most common way to modify the glass transition temperature is to vary the cross-link density. Strengthening the polyurethane network and therefore raising T_g was easily achieved by increasing the index. It was further possible to take advantage of the functionality of various multifunctional compounds to shift the glass transition temperature by adding these compounds. Cross-linking components (functionality > 2) raised the glass transition

temperature, while components having a functionality < 2 lowered the cross-link density. However, an increase of the glass temperature was noticed when adding the monofunctional softening agent benzyl alcohol. At first glance, this seems to be contrary to the theory. Nevertheless, the aromaticity of a polyurethane system also affects the glass temperature of a visco foam and a raising content of aromatic compounds leads to an increase of T_g . An increasing concentration of plasticizers gradually shifted the glass transition to lower temperature. The effect of different additives on the T_g and other foam properties is summarized in table 11.

Table 11. Effect of different additives on several physical properties of viscoelastic polyurethane foam.

Additive	Type of additive	Impact on T_g		Impact on CLD 40% hardness	Impact on porosity	Remarks
		[°C/pphp]	[°F/pphp]	[%/pphp]		
ORTEGOL® G	Cross-linker	+2.8	+5.1	+40	tightens	
ORTEGOL® CXT	Chain extender	+2.0	+3.6	+17	tightens slightly	
ORTEGOL® 204	Cross-linker	-	-	+20	stays constant	makes cells finer
Benzyl alcohol	Softener (f=1)	+1.1	+2.0	-15	opens	destabilizes
ORTEGOL® 315	Softener (f=1)	-3.0	-5.4	-30	opens	
ORTEGOL® 310	Plasticizer	-3.6	-6.5	-20	tightens	promotes shrinkage
TCPP	Plasticizer	-0.6	-1.0	-5	stays constant	

Another option in order to shift the glass transition of a visco foam is to vary the chemical composition of network segments. The glass transition temperature is mainly dependent on the chain length of the used polyols. In a first series of experiments, it was possible to decrease T_g by reducing the mean OH number of the polyol blend. This was achieved by replacing the fundamental cross-linking polyol by an experimental cross-linking polyol with slightly lower OH number. In a second series of experiments, we were even able to reduce the glass transition temperature by changing the chemical structure of the cross-linking polyol, even though the effect was less.

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BIOGRAPHIES

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Dr. Michael Krebs studied chemistry at the University of Stuttgart, Germany and the University Louis Pasteur of Strasbourg, France in a Franco-German double degree course. After completing his studies in France, he received his PhD in organic chemistry in the field of natural product synthesis in 2013. In April 2013, he joined the application technology team of the business line Comfort and Insulation of Evonik Industries as a Technical Manager for Flexible Foam. Among others, his tasks include the development of new foam stabilizers and performance additives. He is in charge of the quality control of Flexible Slabstock Polyurethane Stabilizers and he is technically responsible for Flexible Polyurethane Additives in Africa.

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Dr. Roland Hubel, born in 1972, studied Chemistry at the Ludwig-Maximilians-University of Munich. He received his PhD in Coordination- and Metal organic Chemistry. After working for one year in the field of genetic engineering as civil servant, he joined Degussa Goldschmidt Polyurethane Additives as a research scientist in 2000. After that, he was responsible for R&D of polyethers and development and application technology of additives for microcellular foams. Today he is globally responsible for development and application technology for Flexible Slabstock Polyurethane Additives.

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