Polyurethane Gels

Polyurethane (PU) gels are finding its way into more and more applications where improved comfort and functionality are key requirements. Diverse applications such as biomedical devices, footwear, bicycle saddles and bedding, just to mention a few, have something in common: the increased desire for higher comfort and moisture control. Dow has developed a series of new polymers with such functionality in the form of PU gels. The specific design of the chemical structure, curing rate and final properties can provide additional performance features such as soft touch and moisture control to fulfill the most demanding needs. The purpose of this paper is to discuss the different Dow technologies and developmental systems.

1. Introduction

Polyurethane (PU) elastomers are generally defined as segmented copolymers consisting of soft segments (typically featuring polyether or polyester backbone), and hard segments [1, 2]. The urethane or urea linkages derived from the isocyanate component are the main constituents of the hard segments. Phase separation occurs in these polymers due to the thermodynamic incompatibility between the hard and the soft segments. The extent of the phase separation and the ratio of hard to soft segments have a direct impact on the physical mechanical properties of the PU elastomers [1]. Polyurethane gels may be considered as a special class of polyurethane elastomers, characterized by a very low hardness, namely by a very low ratio of hard to soft segments.

The term "polyurethane gel" would indicate a material that includes a dispersed urethane polymeric network, formed by the reaction of a poly-functional polyol with a poly-functional isocyanate, plus a liquid component that acts as the dispersant for the three-dimensional network structure. This definition is in line with the traditional PU gel technology, which is typically characterized by the presence of a solid elastomeric matrix, combined with a liquid non-reactive component. The non-reactive component acts as plasticizer and is used to soften the PU elastomeric matrix.

Polyurethane gels are materials used in diverse applications such as coatings, absorbent pads and vibration damping inserts, footwear insoles, and electronic component packaging. Versatile and tunable polyurethane chemistry yields gels that have many advantageous properties, such as good pressure-distribution capacity, high shock and shearing-force absorption, and high elasticity and recoverability [1]. All at a very effective cost/performance balance. These properties are highly valued in many different applications, such as bicycle saddles, mouse wrist pads, furniture seating, vibration damping inserts, and footwear insoles.

Naturally, the different applications can require different physical properties. Dow offers a spectrum of polyurethane gel technologies each capable of meeting the needs and property requirements of the application.

This paper describes an overview of Dow's PU gel technology (system A, B, C and D) to develop a range of products capable of meeting the needs of comfort and safety standards, along with gels with moisture control ability, thermal UV stability, containing no plasticizers. Developments include diverse gel formulations ranging from hydrophilic to hydrophobic, clear to opaque, from application in shoe insoles to anti-pressure medical cushions, mouse wrist pads to bicycle saddles.

In addition to an overview of Dow's PU gel technology, this paper outlines the development work that took place within Dow Polyurethane Systems R&D laboratories, and that resulted in a novel PU gel formulation technology (system A and B). The most important difference between the traditional PU gel technology and the novel PU gel technology developed by Dow is that the latter does not require the presence of plasticizers and has additional performance features such as energy dissipation, moisture control to fulfill the most demanding needs of some applications.

Furthermore, the novel PU gel described in this paper is also suitable to be loaded with fillers or pigments or other additives, in order to provide the gel with specific characteristics, such as further improved UV stability and antibacterial properties.

A further advantage of the novel PU gel systems (system A and B) described in this paper is the versatility of the gel technology, lending itself to extensive formulation tailoring. In the present paper, the focus is on the MDI formulation approach. As part of the formulation versatility, it is possible to change the reactivity as well as the physical-mechanical properties such as softness, elasticity, tear and tensile strength over a wide range.

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2. Materials and methods

2.1 Chemicals

All the PU gel systems used for this work are described in table 1. All systems are 100 % solid, formulated two component systems, and featuring polyether backbones. System A and B are MDI-based systems for the manufacturing of very soft and medium soft PU gels respectively. System C is another TDI based system for the manufacturing of PU hydrogel with medium softness. System D is a plasticizer based system for use in specialized applications.

2.2 Methods

Before use, all reactants were degassed. When necessary, polyols were subjected to drying treatment in order to control the water level. Analytical techniques used for the purposes of this work include:

- Isocyanate content (% NCO) measurement according to the dibutylamine titration method (ASTM D 5155)
- Determination of polyol hydroxyl number via titration (ASTM D 4274)
- Measurement of water content in polyols according to the Karl Fischer titration method (ASTM E 203)
- Determination of polyol and isocyanate viscosity using a AR2000 rheometer

2.2.1 Preparation of the isocyanate terminated prepolymers

All the PU gels evaluated for this work were manufactured according to the prepolymer method [4]. The isocyanate terminated prepolymers were prepared by controlled reaction of an excess of isocyanate with the isocyanate reactive compound in a 5-liter reaction vessel equipped with chemicals addition inlet, heating mantle, electrical stirrer, thermometer, and gas inlet/outlet for continuous flow of nitrogen.

The reaction was performed under stirring, feeding the isocyanate reactive compound into the reaction vessel at controlled rate, while maintaining the temperature in the vessel at about 70 – 75 °C. Higher temperatures can cause harmful side reactions that may affect the final performance of the prepolymer. Samples were periodically withdrawn to determine the isocyanate content. After a total reaction time of about 4 h, the isocyanate content was at the theoretical value. The prepolymer was unloaded after stopping the reaction by cooling.

2.2.2 Preparation and testing of the PU gels

Room temperature processing conditions were used for the PU gel samples prepared for this work. Samples were manufactured using Flackteck static mixer as well as hand mixing. In the case of hand mixed samples, vacuum treatment before mixing and after mixing-casting was used to remove the bubbles caused by stirring as well as the dissolved gases. In order to assess the reactivity profile of the PU gels studied for this work, reaction parameters such as gel time were measured. The gel time is measured by the time when a string of the curing polymer can be pulled up from the reactive mixture using a glass rod, and the string does not break for at least 10 s. The samples were manufactured by casting on polymeric film or non adhesive substrates at room temperature. The following ASTM test methods were used in the characterization of the analytical and physical-mechanical properties of the PU gels:

Density was measured according to DIN 53420 and ASTM D 792

Shore hardness was measured as Shore A according to DIN 53505, as well as Shore 00 according to ASTM D 2240. Measurements are performed only on specimens of sufficient thickness to ensure a proper, sensitive test. Generally, for softer material, a thicker sample is preferable. For the purposes of this work, the samples tested had a minimum thickness of at least 10 mm. The hardness of the PU gel is measured on the "naked" gel, after having removed any covering material, if present.

Tear strength was measured according to ASTM D 624 (die C) at 500 mm/min on a suitable tester device. Each data is the average of three measurements. Tear strength was also measured according to DIN 53515 at 500 mm/min on a suitable tester device.

Tensile strength was measured according to ASTM D 412 on a suitable tester device. Each data is the average of five measurements. Tensile strength was also measured according to DIN 53504 on a suitable tester device.

Elongation at break was measured according to ASTM D 412 on a suitable tester device. Each data is the average of five measurements. Elongation at break was also measured according to DIN 53504 on a suitable tester device.

<table>
<thead>
<tr>
<th>Tab. 1: Systems evaluated for the purposes of this work</th>
</tr>
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<tbody>
<tr>
<td>Description</td>
</tr>
<tr>
<td>Key feature</td>
</tr>
<tr>
<td>Polyol (Phase B) viscosity at 23 °C / mPa·s</td>
</tr>
<tr>
<td>Isocyanate viscosity at 23 °C / mPa·s</td>
</tr>
<tr>
<td>Polyol density / g/cm³</td>
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<tr>
<td>Isocyanate density / g/cm³</td>
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</table>
Shape retention properties were measured according to the following procedure: a test specimen having a thickness of at least 10 mm was placed on a metal plate, and then it was bordered with a line. The plate with the specimen was placed in an oven at a fixed temperature, checking at regular intervals whether the specimen had changed its shape and moved over the borderline.

The static compression test set under fixed loading conditions determines the compression set remaining after deformation of a PU gel cushion by loading it for a period of time with a certain load. In this case the applied load was around 0.014 N/mm², and the period of time was 4 days. The test was performed inside a climatic room (22 °C ± 1 °C, at a humidity level of 50 % ± 2 %).

Water uptake was measured according to the following procedure: Dried/conditioned gel samples were cut into 5 cm x 5 cm x 2.5 cm. Weight of gel samples were measured before and after immersion into water until saturation (~21 h). Water uptake was measured using the following formula:

\[
\text{Water uptake %} = \frac{\text{Weight}_{\text{wet}} - \text{Weight}_{\text{dry}}}{\text{Weight}_{\text{dry}}} 
\]

It should be pointed out that, due to very high softness of the materials being tested, the ASTM or DIN test methods for tear, tensile and elongation need to be applied with extreme care in order to maximize the accuracy of the measured properties.

All the physical mechanical properties were measured on PU gel specimens prepared at different index values. The versatility of the novel PU gel formulation approach allows to operating under-index or over-index, corresponding respectively to reacting the isocyanate component with a stoichiometric defect or with a stoichiometric excess of formulated polyol component.

### 3. Results and discussion

#### 3.1 Results

Dow has developed a series of PU gel systems based on different technologies to fulfill the most demanding needs of diverse applications such as biomedical devices, footwear, bicycle saddles and bedding. A brief overview of Dows PU gel technologies and their properties is given below (tab. 2).

#### 3.1.1 System A: Non-plasticizer gel technology [1]

This novel PU gel formulation technology allows to successfully combining elevated softness with a good level of physical-mechanical properties while maintaining a plasticizer-free environment. In order to achieve the required softness and visco-elasticity properties, some of the traditional PU gel materials need to be manufactured around 40–70 index. This means that the working ratio is such that only 40–70 % of the OH groups that are present in the isocyanate reactive component are reacted. On the other hand, the novel PU gel technology described in this paper allows manufacturing of good performing PU gel material even when operating at perfect stoichiometry (isocyanate index 100). Therefore, the novel PU gel technology is preferably to be applied at isocyanate index 100, since this is expected to maximize the final physical-mechanical properties. Furthermore, when operating a low-index reaction (isocyanate component with stoichiometric excess of polyol component), the PU gel may contain some non-reacted polyol or some low MW urethane-polyol derivatives. The presence of all these derivatives is instead minimized when manufacturing the PU gel at isocyanate index 100.

#### 3.1.2 System B: Non-plasticizer, moisture control gel technology

Gels are typically soft to the touch, can be molded, and are capable of bearing a load. Gels can be used in cushioning and padding applications, and as such find use in articles such as bicycle seats, shoe inserts, and glove padding. In addition to comfort or cushioning, there is also a need for a material having improved moisture control, non-leaching gel technology. This technology gives us the flexibility to tailor the features such as hydrophilicity, softness, transparency, UV stability yet having no toxic leachable additives, and desirable physical properties commonly conferred by surfactants or other additives. The water holding, moisture transport capacity of these gels arise mainly due to the presence of hydrophilic groups in the polymer chains. Dow has developed this novel PU gel technology approach that allows manufacturers to prepare PU gels combining high elasticity with very high softness, as well as excellent shape retention, and efficient moisture control properties.

<table>
<thead>
<tr>
<th>Description/features</th>
<th>System A Non-plasticizer gel</th>
<th>System B Non-plasticizer moisture control gel</th>
<th>System C Hydrogel technology</th>
<th>System D Plasticizer based gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td>2K</td>
<td>2K</td>
<td>2K</td>
<td>2K</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Curing</td>
<td>Ambient temperature</td>
<td>Ambient temperature</td>
<td>Ambient temperature</td>
<td>Ambient temperature</td>
</tr>
<tr>
<td>Stickiness</td>
<td>High</td>
<td>Low</td>
<td>No</td>
<td>High</td>
</tr>
<tr>
<td>Optical transparency</td>
<td>Clear</td>
<td>Clear to opaque</td>
<td>Clear to opaque</td>
<td>Clear</td>
</tr>
<tr>
<td>Hydrophilicity</td>
<td>Hydrophobic</td>
<td>Hydrophilicity can be tailored</td>
<td>Hydrophobic</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>Thermal/dimensional stability</td>
<td>High</td>
<td>High</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Moisture transfer/wicking</td>
<td>Low</td>
<td>High/low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Hardness/Shore O0</td>
<td>–30</td>
<td>22–40</td>
<td>19–30</td>
<td>19–30</td>
</tr>
<tr>
<td>Tensile/kPa</td>
<td>–1.4–207</td>
<td>–221</td>
<td>–241</td>
<td>–241</td>
</tr>
<tr>
<td>Elongation/%</td>
<td>450–600</td>
<td>400</td>
<td>158–200</td>
<td>600</td>
</tr>
<tr>
<td>Tear Strength/kN/m</td>
<td>–0.88</td>
<td>0.70–0.96</td>
<td>–0.42</td>
<td>–0.68</td>
</tr>
</tbody>
</table>
3.1.3 System C: Hydrogel technology [1, 2]

Hydrogel is a crosslinked macro molecular network made of hydrophilic polymers, capable of containing a very high amount of water (>95% of its overall weight). It is a two phase system composed of the polymeric network and the water phase absorbed. The 3D structure swells by absorbing water thanks to the hydrophilic functions available. The hydrogel volume increases, keeping its shape and without breaking up. A hydrogel is not soluble in water. PU hydrogels are made from Dow’s proprietary Hypol technology. Polymer chains in hydrogels are linked in two ways, either permanent cross linking (chemical gel) or reversible cross linking by van der Waals interactions and hydrogen bonding (physical gel).

3.1.4 System D: Plasticizer based gel technology

This technology is in line with the traditional PU gel technology, which is typically characterized by the presence of a solid elastomeric matrix, combined with a liquid non-reactive component. The non-reactive component acts as plasticizer and is used to soften the PU elastomeric matrix. The plasticizers utilized in this development are non-toxic. The polyurethane component of the gel, under the most preferred circumstances, couples to the non-volatile organic liquid by secondary bonding forces, such as hydrogen bonding and van der Waals interactions in order to form a completely compatible plasticized gel in which the non-volatile liquid components are bound and do not migrate or exude during use.

3.2 Discussion

3.2.1 Mechanical properties of different PU gel systems

The resultant two-phase micro-domain structure exhibited by polyurethane elastomers due to thermodynamic immiscibility between the hard urethane segments and the soft polyol segments is responsible for the superior mechanical properties of PU elastomers. In addition to phase separation, the physical-mechanical properties of PU elastomers are largely dependent on the ratio of hard to soft segments. In the case of PU gels, the need to achieve very high softness means that the amount of hard segments must be minimized.

In our experimental studies, it was recognized that the viscoelastic and physical-mechanical properties depend on the cross linking, gel structure elastically active crosslinks, network chains, dangling chains, on their size and composition [1]. PU gels were designed with linear or branched network, few long or many dangling chain ends, hydrophilic or hydrophobic groups, varying crosslinking density to understand how their properties and performance differs. The key logic was to understand the co-relationship of structure, property and process to design systems based on specific application needs.

Table 2 reports physical mechanical properties measured for the selected four PU gel systems considered in this study. The reactivity at which the samples were manufactured is not specified, since the reactivity was easily adjusted by changing the catalyst level in the polyol. The reactivity also depends on the temperature of the components. The suggested temperature range is 25 – 45 °C. The four PU gel systems described in Table 2 have medium to very low hardness. System A and B showed relatively lower elongation at break compared to system D, but tensile strength values were comparable with system D. The novel PU gel formulation technology approach (system B) described in this paper allows to successfully combining an elevated softness with a good level of physical-mechanical properties, while maintaining the specific needs of certain applications like moisture control. System C showed relatively low tensile strength and elongation properties. PU hydrogels are weak polymer networks as indicated by the low numbers on the strength properties, whereas system D exhibited very high tensile strength and elongation at break.

Any PU elastomer system tends to show some sensitivity to stoichiometry, meaning that the physical mechanical properties are influenced by the ratio of reactive groups in the reactive mixture [4]. This is also true in the case of PU gels. In order to achieve the target softness and visco-elasticity properties of specific applications, PU gel materials were manufactured at varying index 25–60.

Fig. 1: Relationship of index and tensile, tear properties of specific gel systems (system B)

Fig. 2: Relationship between index and hardness (Shore OO) of specific PU gel systems (system B)
On the other hand, the novel PU gel technology described in this paper (system A and B) allows to manufacturing good performing PU gel material even when operating at perfect stoichiometry (isocyanate index 100).

Formation of crosslinked network in PU leads to a decrease in the molecular mobility and flexibility and causes an increase in modulus of elasticity and tensile strength, as well as increases $T_g$ of PU, but on the other hand decreases elongation at break [1]. In the current study, similar behaviour was observed for our gel systems.

Figure 1 and 2 show the relationship between the hardness, tensile properties and the isocyanate index for specific gel systems (system B). If the isocyanate index increases, that is, the isocyanate ratio over polyol in polyurethane increases, the gel hardness and tensile strength also increases in a linear pattern. As shown in figure 1, below the critical index (~25) the mechanical properties are poor (low tensile strength and low % elongation at break). As the index increases, the tensile strength increases and elongation decreases due to increased crosslinking and decrease in the molecular mobility.

The isocyanate index can usually be used to give an indication of the hard-segment ratio in gels. The relationship curve that we obtained could be used to predict and estimate the final hardness of the gel from the hard-segment/soft-segment composition ratio for particular applications.

3.2.2 Shape retention and compression set properties

PU gels are non-perfect elastomers, which may be described as visco-elastic materials. The elevated softness corresponds to an elevated viscosity component within the visco-elasticity balance. Particularly super soft PU gels (0 Shore 00) and “traditional” PU gels containing plasticizers or other non-reactive components may behave more as a liquid than a solid material. In practical terms, this means that the PU gel may be unable to maintain its dimensional stability, and its shape will change with the passing of time. Applying a load and/or subjecting the PU gel to treatment at elevated temperature may accelerate this shape change phenomenon.

Systems A, B, C, and D were tested according to the shape retention/dimensional stability test described previously. Table 3 reports the corresponding results, which show that the novel PU gel A and B described in the paper features an outstanding degree of shape retention properties, even when manufactured at very low hardness. These novel gels, as detailed in the previous paragraph, also have...
3.2.3 Gelation and reactivity

System reactivity depends on several factors: polyol reactivity, isocyanate reactivity, acid/base balance, catalyst type and loading, temperature and crosslinker type. System reactivity is very important for several reasons: handling time, tack-free time, and because the morphology of the system can organize differently depending on how quickly it reacts. A slower reacting system may react so slow that there is too much phase separation between the polyol soft segment and the growing urethane hard segment. Depending on the system, it may not be visible immediately, but mechanical properties could suffer.

The gel properties of polyurethanes depend on the gelation condition as well as the composition (index, functionality). The curing conditions for gelation can be adjusted to obtain an optimized relationship between the gelation rate, catalyst concentration, and gel properties. As shown in figure 3, as the amount of catalyst increases, the curing time decreases gradually in an inverse proportional pattern. Under the gelation conditions we chose, the curing rate and time thus could be controlled by a change in the catalyst concentration.

In addition to catalyst concentration, the reactivity of the system is sensitive to index. In figure 4 shows the relationship between pot life, gel time and cure time versus the isocyanate index for gel system B. If the index of the gel system is below a critical value, it does not gel or it takes a very long time to gel. For instance in the current specific gel system, the critical index value was ~25 above which a good network is formed. Formation of PU network at ~25 index was further supported by testing the mechanical properties (tensile, % elongation, tear strength) of the gel systems at different index ratios (fig. 1).

The functionality or average functionality of a polyol should be taken into consideration in designing the proper gel formulation for producing polyurethane gels. Figure 5 shows the relationship between hardness, tensile, tear properties versus the polyol functionality for gel systems B. In one non-limiting embodiment, the use of low functionality polyol (about ≤2) was useful for the production of viscoelastic gel. When low functionality polyols were used, a higher isocyanate index was generally required or else the network does not form.

3.2.4 Moisture uptake

Hydrophilic gels are formed when a three dimensional polymeric network is loosely cross-linked. They swell in water but do not dissolve in it. The water holding capacity of the hydrogels arises mainly due to the presence of hydrophilic groups in the polymer chains. The water holding capacity of a hydrophilic gel is dependent on the number of the hydrophilic groups, index and crosslinking density. Moreover, the secondary weak forces or intermolecular forces between polymer chains play very important role in water holding capacity of gels. The intermolecular forces (attractions) are H-bonding, London dispersion forces, permanent dipol interactions, ionic bond interactions and van der Waals forces. They can be expressed as CED (cohesive energy density).

In the current study, different gel systems were designed with different functionality, hydrophilicity and index to understand the water transport properties of the gel systems for applications demanding moisture control. The influence of hydrophilicity and index on water uptake is shown in figure 6 and 7. With higher number of the hydrophilic...
groups the water holding capacity is higher (fig. 6), while with an increase in the index there is a decrease in the equilibrium swelling due to the decrease in the hydrophilic groups and increased cross-linking (fig. 7). Again, for very low index systems (< 26) water uptake was low due to lack of network formation.

4. Conclusion

Dow has developed a series of PU gel systems based on different technologies for diverse applications such as biomedical devices, footwear, bicycle saddles and bedding. The specific design of the chemical structure, reactivity and final properties provided additional performance features such as soft touch, moisture control to fulfill the most demanding needs. These novel PU gel systems can be processed according to casting technology using suitable low-pressure machines. The most important novelty aspect of the new PU gel technology is the possibility of manufacturing items that are completely free of plasticizers with additional performance features such as moisture control. Overall, the Dow gel systems presented in this work could be set among the most comfortable, high performance gels.

5. References