PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{7} **:**
C08G 18/48, 18/12

A1

(11) International Publication Number: **WO 00/18817**

(43) International Publication Date: 6 April 2000 (06.04.00)

(21) International Application Number: PCT/EP99/05375

(22) International Filing Date: 27 July 1999 (27.07.99)

(30) Priority Data:
09/160,968 25 September 1998 (25.09.98) US

(71) Applicant *(for all designated States except MN)*: ARCO CHEMICAL TECHNOLOGY, L.P. [US/US]; Suite 238, Two Greenville Crossing, 4001 Kennet Pike, Greevnville, DE 19807 (US).

(71) Applicant *(for MN only)*: LYONDELL CHEMIE TECHNOLOGIE NEDERLAND B.V. [NL/NL]; Theemsweg 14, NL-3197 KM Botlek Rotterdam (NL).

(72) Inventor: HO, David, J.; 197 Daylesford Boulevard, Berwyn, PA 19312 (US).

(74) Agent: COLMER, Stephen, Gary; Mathys & Squire, 100 Gray's Inn Road, London WC1X 8AL, United Kingdom (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PROCESS FOR MAKING MICROCELLULAR POLYURETHANE ELASTOMERS

(57) Abstract

Microcellular elastomers and a process for making them are disclosed. The process comprises reacting a resin component ("B" side) with an isocyanate-terminated prepolymer ("A" side). Pre-reacting the right proportion of chain extender into an "A" side that also includes a high-primary, low-unsaturation polyol is the key to making low-density (less than 0.5 g/cm^3) microcellular elastomers while avoiding problems with poor processing or inferior physical properties. The process is easy to practice, and provides lighter, high-quality polyurethane products, including protective sports equipment, arm rests or steering wheels for the auto industry, and midsoles or shoe soles for footwear.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

PROCESS FOR MAKING MICROCELLULAR POLYURETHANE ELASTOMERS

FIELD OF THE INVENTION

The invention relates to microcellular polyurethane elastomers and a process for making them. The elastomers are valuable for a variety of uses, most notably in automotive applications and footwear.

BACKGROUND OF THE INVENTION

Microcellular polyurethane elastomers are well known. They have fine, evenly distributed cells, and densities that are low compared with solid urethane elastomers yet high compared with flexible polyurethane foam. Microcellular polyurethane elastomers are used in automotive parts (e.g., bumpers and armrests), gaskets, vibration damping applications, and footwear.

While many ways to make microcellular polyurethane elastomers have been revealed, most approaches fit into two categories: the "one-shot" method and the "prepolymer" method. In the one-shot method, all of the components (polyols, polyisocyanate, blowing agents, surfactant, catalyst, chain extenders) are combined and reacted in a single step. In contrast, the prepolymer approach pre-reacts the polyisocyanate with a polyol to make a "prepolymer" (the "A" side) that is subsequently combined with the remaining reactants including any chain extenders (the "B" side), in a second step to make the elastomer. As U.S. Pat. No. 4,559,366 illustrates, it can be beneficial to make a "quasiprepolymer" by using an by reacting the polyol with enough polyisocyanate to produce a mixture of isocyanate-terminated prepolymer and free polyisocyanate. Such quasiprepolymers are commonly used to boost the available NCO content of the "A" side.

It is also known to prepare prepolymers ("A" sides) from isocyanates and polyol-chain extender mixtures. For example, U.S. Pat. No. 5,658,959 teaches to make an isocyanate-terminated prepolymer from MDI, dipropylene glycol, a polyoxypropylated/ethoxylated glycerine, and a polyoxypropylated/ethoxylated glycol (see Example 1). The reference polyols have up to 35 wt.% of ethylene oxide content, but an undisclosed degree of "endcapping" or primary hydroxyl group content (see column 5, lines 17-38). The reference is also silent regarding the unsaturation level of the polyols. U.S. Pat. No. 5,618,967 contains a similar disclosure. In sum, these references suggest that neither the unsaturation level nor the primary hydroxyl content of the polyols is important.

U.S. Pat. No. 5,284,880 also shows (see, e.g., column 13, lines 30-45) a prepolymer made from an isocyanate, a polyol, and a chain extender (dipropylene glycol). This reference teaches, however, that the "A" side polyol must be a "polyether containing predominately secondary hydroxyl groups" (see Abstract; col. 2, lines 4-5; and col. 4, lines 28-54). This reference is also silent regarding any need for a low-unsaturation polyol.

The benefits of polyols with low levels of unsaturation (<0.020 meq/g) for polyurethanes generally and for microcellular polyurethane elastomers in particular are known. U.S. Pat. Nos. 5,677,413 and 5,728,745, for example, describe microcellular polyurethanes made from polyols having unsaturations less than about 0.010 meq/g. The '745 patent makes the elastomers by either the prepolymer method (see Example 8 and Table 6 of the reference) or by the one-shot approach (see Examples 9-11 and Table 8 of the reference). The prepolymers of Example 8 are reaction products of polyoxypropylene diols or triols with 4,4'-MDI. No chain extender is used to make the prepolymer. In Examples 9-11, high-primary, low-unsaturation polyols are used. The references teach several advantages of using low-unsaturation polyols, including good resilience, low compression set, and reduced shrinkage; these advantages are particularly important for shoe soles.

U.S. Pat. No. 5,106,874 teaches prepolymer and one-shot approaches to making noncellular elastomers from low-unsaturation polyols. The prepolymers are generally made by reacting polyoxyalkylene polyols with an excess of polyisocyanate. The reference teaches that chain extenders can be included in the prepolymer (column 7, lines 49-52). However, none of the actual examples includes a chain extender reacted into the "A" side, and no microcellular elastomers are made.

U.S. Pat. No. 5,696,221 teaches to make polyurethane/urea elastomers by reacting prepolymers with a chain extender. The prepolymers include a diol having a molecular weight less than 400 in addition to a low-unsaturation, polyoxypropylene diol. The reference does not disclose microcellular elastomers.

Despite the well-recognized benefits of using low-unsaturation polyols in formulating microcellular polyurethane elastomers, some problems remain with the conventional one-shot and prepolymer approaches. As noted in U.S. Pat. No. 4,559,366, the one-shot approach cannot easily be used with 4,4'-diphenylmethane diisocyanate (4,4'-MDI), a ubiquitous raw material for shoe sole elastomers, because it is not readily miscible with other reactants, and it solidifies at room temperature (see col. 1 of the reference).

The prepolymer approach, however, also has drawbacks. Formulating high-quality, low-density elastomers, especially ones that have densities less than 0.5 g/cm^3, is difficult. An obvious way to reduce density is to increase the amount of blowing agent (usually water). However, this increases the urea content of the elastomer, reduces elongation, and reduces flexibility. Adding more chain extender into the "B" side helps to maintain good hardness at lower densities, but this can cause poor processability and premature phase separation. As Comparative Example 8 (below) shows, such products often have an undesirable incidence of surface defects and internal splitting.

While it is known to include some chain extender in the "A" side, little or nothing is known about the benefits of doing so in the context of making microcellular elastomers based on low-unsaturation polyols, particularly those having a high content of primary hydroxyl groups.

In sum, the industry would benefit from better ways to make microcellular polyurethane elastomers, especially low-density elastomers. A preferred approach would use the low-unsaturation polyols now known to confer significant physical property advantages to urethanes. A valuable process would be easy to practice, yet would overcome the drawbacks of the conventional one-shot and prepolymer methods, particularly in formulating low-density elastomers.

SUMMARY OF THE INVENTION

The invention is a breakthrough process that enables formulators of microcellular elastomers to achieve densities below 0.5 g/cm^3 without sacrificing good processing latitude or excellent elastomer properties. The process comprises reacting a resin component ("B" side) with an isocyanate-terminated prepolymer ("A" side), optionally in the presence of a blowing agent, a surfactant, and a catalyst. The resin component includes a first chain extender and a first high-primary, low-unsaturation polyol. The key component, however, is the prepolymer, which is made by reacting a polyisocyanate, a second high-primary, low-unsaturation polyol, and a second chain extender. The second chain extender reacted into the "A" side comprises from about 5 to about 60 equivalent percent of the total chain extender.

I surprisingly found that pre-reacting the right proportion of a chain extender component into an "A" side that also includes a high-primary, low-unsaturation polyol as part of the prepolymer is the key to making low-density (less than 0.5 g/cm^3) microcellular elastomers while avoiding problems with poor processing or inferior physical properties. The process is easy to practice, and provides lighter, high-quality polyurethane products, including protective sports equipment, arm rests or steering wheels for the auto industry, and midsoles or shoe soles for footwear.

DETAILED DESCRIPTION OF THE INVENTION

In the process of the invention, the resin component ("B" side) comprises a first high-primary, low-unsaturation polyol, and a chain extender.

Polyols useful in the process of the invention are prepared by ring-opening polymerization of cyclic ethers, and include epoxide polymers, oxetane polymers, tetrahydrofuran polymers, and the like. The polyols can be made by any desired method; however, the ultimate product must have both low unsaturation and a high content of primary hydroxyl groups. Preferred are polyether polyols made by polymerizing epoxides, especially propylene oxide and/or ethylene oxide. Particularly preferred are propylene oxide-based polyols that are capped or tipped with oxyethylene groups.

The polyol has a high content of primary hydroxyl end groups. Such polyols are normally made by tipping or capping the ends of an polyoxypropylene polyol with oxyethylene units. By "high-primary," we mean polyols having at least about 50% primary hydroxyl groups. More preferably, the polyols have at least about 65% primary hydroxyl groups; most preferred are polyols having at least about 75% primary hydroxyl groups. High primary hydroxyl group content is important; as Comparative Example 6 below shows, poor elastomers result when a low-primary polyol is used in the process of the invention.

The polyol also has low unsaturation. By "low-unsaturation," we mean less than about 0.02 meq/g of unsaturation as measured by standard methods, such as ASTM D-2849-69, "Testing of Urethane Foam Polyol Raw Materials." Preferred polyols have unsaturations less than about 0.01 meq/g; most preferred are polyols having unsaturations less than about 0.007 meq/g. Polyols with very low unsaturation levels are conveniently made via double metal cyanide catalysis as described, for example, in U.S. Pat. Nos. 5,470,813 and 5,482,908, the teachings of which are incorporated herein by reference.

The polyol preferably has an average hydroxyl functionality less than about 3. A more preferred range is from about 1.8 to about 3.0. In *addition, the polyol preferably has a number average molecular weight* within the range of about 500 to about 50,000. A more preferred range is from about 1000 to about 6000; most preferred is the range from about 2000 to about 6000.

The polyol preferably has an oxyethylene content of at least about 5 wt.%, more preferably from about 10 to about 20 wt.%, which can be present internally, as a tip, or as an endcap. Preferably, most of the oxyethylene content is located toward the end of the polyol to provide for the desirable high content of primary hydroxyl groups.

The high-primary, low-unsaturation polyol is typically the major component of the "B" side. Generally, it comprises at least about 40 wt.% of the resin component. A preferred range is from about 45 to about 90 wt.%, more preferably from about 50 to about 70 wt.% of the resin component.

The resin component also includes a chain extender. Useful chain extenders have at least two active hydrogens, and include low molecular weight diols, diamines, aminoalcohols, dithiols, or the like. Preferably, the chain extenders have number average molecular weights less than about 400, more preferably less than about 300. Diols are preferred chain extenders. Suitable chain extenders include, for example, ethylene glycol, propylene glycol, 2-methyl-1,3-propanediol, 1,4-butanediol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, neopentyl glycol, cyclohexanedimethanol, 1,6-hexanediol, ethylene diamine, ethanedithiol, and the like, and mixtures thereof. Particularly preferred are *dipropylene glycol, ethylene glycol, and* 1,4-*butanediol*. A minor proportion of chain extender having 3 or more active hydrogens (e.g., glycerine) can be included if desired.

The chain extender is a minor "B" side component. Typically, it comprises less than about 30 wt.% of the resin component. A preferred range is from about 1 to about 20 wt.%, more preferably from about 3 to about 10 wt.% of the resin component.

The resin component optionally includes additional polyols, which may or may not be low-unsaturation or high-primary polyols. Preferably, the resin component includes a polymer polyol. Suitable polymer polyols include the well-known variety prepared by in situ polymerization of vinyl monomers in a base polyol to give a stable dispersion of polymer particles in the base polyol, such as styrene-acrylonitrile (SAN) polymer polyols. Other suitable polymer polyols include PIPA and PHD polyols, which are--like the SAN polymer polyols--commercially available. These polymer *polyols have polymer solids contents generally in the range of about* 5 *to* about 50 wt.%. When a polymer polyol is included, it is preferred to use an amount within the range of 5 to about 45 wt.% based on the total amount of resin component.

An isocyanate-terminated prepolymer ("A" side) reacts with the resin component ("B" side) in the process of the invention. The prepolymer is the reaction product of a polyisocyanate, a second high-primary, low-unsaturation polyol, and a second chain extender.

The polyisocyanate is an aromatic, aliphatic, or cycloaliphatic isocyanate that contains at least two free NCO groups. Suitable polyisocyanates include diphenylmethane diisocyanates (MDIs), polymeric MDIs, MDI variants, toluene diisocyanates, hexamethylene diisocyanate, isophorone diisocyanate, and the like, and mixtures thereof. Preferred polyisocyanates are 4,4'-MDI, other MDI blends that contain a substantial proportion of the 4,4'-MDI isomer, and modified MDIs made by reacting MDI with itself of another component to introduce carbodiimide, allophanate, urea, urethane, biuret, or other linkages into the structure (MDI variants). Particularly preferred are 4,4'-MDI, carbodiimide-modified MDIs, and mixtures thereof. The amount of polyisocyanate used is preferably the amount needed to give an NCO-terminated prepolymer or quasiprepolymer having a free NCO content within the range of about 15 to about 30 wt.%, more preferably from about 20 to about 28 wt.%.

The prepolymer includes a second high-primary, low-unsaturation polyol, which may be the same as or different from the first high-primary, low-unsaturation polyol. The second polyol has the same general characteristics as the first, however, i.e., low unsaturation (less than about 0.02 meq/g) and a high content (at least about 50%) of primary hydroxyl groups. The high-primary, low-unsaturation polyol is a minor "A" side component. The isocyanate-terminated prepolymer preferably comprises from about 1 to about 10 wt.% of the prepolymer component; a more preferred range is from about 2 to about 8 wt.%.

The prepolymer also includes a chain extender. This chain extender (the "second" chain extender) may be the same as or different from the chain extender used in the resin component (the "first" chain extender). Otherwise, the second chain extender fits the above description of the first chain extender. The second chain extender, which is reacted into the "A" side, comprises from about 5 to about 60 equivalent percent of the total chain extender. Preferably, the second chain extender comprises from about 10 to about 40 equivalent percent of the total chain extender; a most preferred range is from about 15 to about 35 equivalent percent.

The amount of chain extender used to make the prepolymer is important. If less than about 5 equivalent percent is present, foam splitting, surface defects, and other problems result (see Comparative

Example 8). On the other hand, if more than about 60 equivalent percent of the total chain extender is present in the "A" side, excessive heat can be generated, which can lead to unwanted gellation of the prepolymer.

While most prepolymers are simply reaction products of a polyisocyanate and a polyol, the present invention incorporates a chain extender into the prepolymer. I surprisingly found that pre-reacting 5 to 60 equivalent percent of the total chain extender into the "A" side, in combination with using a high-primary, low-unsaturation polyol, is the key to making low-density (less than 0.5 g/cm^3) microcellular elastomers while avoiding problems with poor processing or inferior physical properties. This simple step is crucial for providing lighter, high-quality polyurethane products, particularly midsoles or shoe soles for footwear.

The prepolymer is generally made by combining the second polyol, second chain extender, and polyisocyanate in any desired order, and heating the mixture at a temperature and for a time effective to produce an isocyanate-terminated prepolymer. Usually, it is preferred to react the polyisocyanate and the high-primary, low-unsaturation polyol together for a short time before introducing the second chain extender. Heating then continues until the prepolymer reaches the desired content of free NCO groups. In another preferred mode, all or part of the second chain extender is included at the start of the prepolymer-forming reaction.

After the prepolymer has been made, it is combined with the resin component using conventional techniques to make the microcellular elastomer. The resin component is a well-blended mixture of the first low unsaturation polyol, the first chain extender, and other optional components such as blowing agents, surfactant, catalysts, and the like. The elastomers can be made by hand casting or machine. The "A" and "B" side components are combined, rapidly mixed, and injected or poured into open or closed molds. The formulations described herein are well suited for use with commercial equipment (such as the Gusbi molding machine) for making midsoles and shoe soles by closed molding techniques.

Preferably, the process of the invention is performed in the presence of a blowing agent. Suitable blowing agents are those well known in the art of formulating microcellular polyurethane elastomers. They include "physical" blowing agents, such as low-boiling halocarbons (e.g., CFCs, HCFCs, methylene chloride) or hydrocarbons (e.g., butane, pentane), inert gases (e.g., nitrogen, argon, carbon dioxide), or the like, and "reactive" blowing agents, such as water and other active-hydrogen compounds that react with NCO groups to liberate gases. Mixtures of blowing agents can be used. Water is a particularly preferred blowing agent. The blowing agent is used in an amount needed to produce a microcellular elastomer having a density of less than 0.5 g/cm^3. Preferably, the resulting elastomer has a density within the range of about 0.02 to about 0.4 g/cm^3; most preferred is the range from about 0.1 to about 0.3 g/cm^3.

The process optionally includes other conventional urethane foam components, such as surfactants, blowing catalysts, urethane-forming catalysts, pigments, UV stabilizers, crosslinkers, antioxidants, other polyols, and/or other additives. These optional ingredients are preferably mixed thoroughly with the resin component before reacting it with the "A" side to make the elastomer.

The process of the invention offers advantages for elastomer processing. "Moving" the right amount of chain extender into the "A" side component gives improved control over reactivity and flowability during elastomer processing because a significant fraction of the total reaction happens before the elastomer is formulated. The process also offers wide processing latitude. As the examples below demonstrate, excellent products can be made over a broad temperature range (40-60°C) and a broad index range (95 to 105), and demold times are short (< 7 min).

The process also offers physical property advantages. In the past, it was difficult to make microcellular elastomers with densities less than 0.5 g/cm^3 (especially ones with densities less than 0.3 g/cm^3) while avoiding problems with product quality. Microcellular elastomers made using the process of the invention have excellent tensile and tear strength, good skin quality, and no internal splits. As the examples below show, the process of the invention makes it possible to formulate--with ease--excellent elastomers having densities as low as about 0.26 g/cm^3.

The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

EXAMPLES 1-5 and COMPARATIVE EXAMPLE 6

Preparation of Microcellular Polyurethane Elastomers

A Gusbi machine is used to mold 10-mm microelastomer plaques by reaction injection molding mixtures of the "A" and "B"-side components described below at 35°C. Mold temperatures are in the 40-60°C range. The products are tack-free in less than one minute. Physical properties appear in Table 1.

As the table shows, microcellular elastomers with densities less than 0.27 g/cm^3 and an excellent balance of properties are available from the process of invention. In each example of the invention, the "A" side includes a chain extender (dipropylene glycol) and a high-primary, low-unsaturation polyol. Comparative Example 6 demonstrates the importance of using a "high-primary" polyol. Low unsaturation alone is not enough to give good products at such low densities.

Formulation

Resin component ("B" side)	pbw
Low-unsaturation polyol (see Table 1)	58
Polymer polyol[1]	35
Water	1.1
Ethylene glycol	5.2
Dabco EG catalyst[2]	0.2
X-8154 catalyst[2]	1.0
BL-17 catalyst[2]	0.2
T-120 catalyst[2]	0.02
DC-193 surfactant[3]	0.25
LK-221 emulsifier[2]	0.75
Pigment (e.g., carbon black or TiO_2)	1.2
B-75 stabilizer[4]	1.0
Prepolymer ("A" side; 24 wt.% NCO)	
4,4'-MDI	80
Carbodiimide-modified MDI	8
Low-unsaturation polyol (see Table 1)	5
Dipropylene glycol	7

---

[1] SAN-type, 43 wt.% solids content, hydroxyl number 20 mg KOH/g

[2] product of Air Products; [3] product of Dow Corning; [4] product of Ciba-Geigy.

Table 1. Microcellular Polyurethane Elastomers

Example	1	2	3	4	5	C6
Resin polyol	A-4220	A-4220	A-4220	A-2220	A-4220	A-3201
Prepolymer polyol	A-4220	A-4220	A-4220	A-2220	A-2220	A-3201
A/B side (w/w)	0.53	0.55	0.58	0.55	0.55	0.55
Index (NCO/OH)	0.95	1.00	1.05	1.00	1.00	1.00
Physical Properties						
Density (g/cm^3)	0.265	0.265	0.265	0.265	0.265	0.265
Hardness (Asker C)	61	62	62	60	60	58
Tensile strength (kg/cm^2)	19.4	20.8	23.2	16.4	19.2	*
Elongation (%)	307	255	296	319	324	*
Split tear (kg/cm, 10 mm)	2.3	2.6	2.6	1.9	2.1	*

A-4220 is Accuflex 4220 polyol, a polyoxypropylene diol having Mn=4000, about 20 wt.% oxyethylene content (5% internal, 15% cap), and a primary hydroxyl group content of about 85%; A-2220 is Accuflex 2220 polyol, a polyoxypropylene diol having Mn=2000, about 20 wt.% oxyethylene content (5% internal, 15% cap), and a primary hydroxyl group content of about 85%; A-3201 is Accuflex 3201 polyol, a polyoxypropylene diol having Mn=3000, about 10 wt.% internal oxyethylene content; all are products of ARCO Chemical.

* Sample cracks and cannot be tested.

EXAMPLE 7

The procedure of Examples 1-5 is followed, except that the prepolymer is made using 52 parts of 4,4'-MDI, 4 parts of dipropylene glycol, and 3 parts of Accuflex 4220 polyol.

The resulting midsoles, which can be molded easily over a broad temperature range of 40 to 60°C, are excellent. Physical properties: density: 0.26 g/cm^3; Asker C hardness: 60-65; split tear strength: 2.0 kg/cm; tensile strength: 19 kg/cm^2. Demold time is less than 7 min., and no skin peeling or internal splitting is evident.

COMPARATIVE EXAMPLE 8

In this example, all of the chain extender to be used is included in the resin component ("B" side).

The procedure of Example 7 is followed, with the following changes. The resin blend contains 1.5 parts of water and 12.5 parts of ethylene glycol. The prepolymer is made using 81 parts of 4,4'-MDI, 46 parts of Accuflex 4220 polyol, and no chain extender.

The resulting midsoles are poor. Physical properties: density: 0.26 g/cm^3; Asker C hardness: 60-65; split tear strength: 1.6 kg/cm; tensile strength: 17 kg/cm^2. Demold time is 7 min. or more. Many of the samples have poor skin quality, which is evident upon demolding. In addition, many of the parts have internal splits.

The preceding examples are meant only as illustrations; the following claims define the scope of the invention.

CLAIMS

1. A process which comprises reacting a resin component ("B" side) with an isocyanate-terminated prepolymer ("A" side), optionally in the presence of a blowing agent, a surfactant, and a catalyst, to produce a microcellular polyurethane elastomer having a density less than 500 kg/m^3;

wherein the resin component comprises a mixture of a first chain extender and a first high-primary, low unsaturation polyol;

wherein the prepolymer is made by reacting a polyisocyanate, a second high-primary, low-unsaturation polyol, which may be the same as or different from the first polyol, and a second chain extender, which may be the same as or different from the first chain extender; and

wherein the second chain extender reacted into the "A" side comprises from 5 to 60 equivalent percent of the total chain extender.

2. The process of claim 1 wherein the second chain extender comprises from 10 to 40 equivalent percent of the total chain extender.

3. A microcellular polyurethane elastomer which comprises the reaction product of:

(a) a resin component ("B" side) comprising a mixture of:

(i) a first high-primary, low-unsaturation polyol;

(ii) a first chain extender; and

(iii) optionally, a blowing agent, a surfactant, and a catalyst; and

(b) an isocyanate-terminated prepolymer ("A" side) comprising the reaction product of:

(i) a polyisocyanate;

(ii) a second high-primary, low-unsaturation polyol, which may be the same as or different from the first polyol; and

(iii) a second chain extender, which may be the same as or different from the first chain extender;

wherein the second chain extender reacted into the "A" side comprises from 5 to 60 equivalent percent of the total chain extender; and

wherein the elastomer has a density less than 500 kg/m^3.

4. The elastomer of claim 3 having a density within the range of 20 to 400 kg/m^3.

5. The elastomer of claim 3 or 4 wherein the "B" side includes a polymer polyol.

6. The elastomer of claim 3, 4 or 5 wherein the blowing agent is water.

7. The elastomer of any of claims 3 to 6 wherein the polyisocyanate comprises a mixture of a major proportion of 4,4'-MDI and a minor proportion of carbodiimide-modified MDI.

8. The elastomer of any of claims 3 to 7 wherein one or both of the polyols have a primary hydroxyl end group contents greater than 75% and unsaturation levels of less than 0.007 meq/g.

9. The elastomer of any of claims 3 to 8 wherein the second chain extender comprises from 10 to 40 equivalent percent of the total chain extender.

10. The elastomer of any of claims 3 to 9 wherein one or both chain extenders are selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, ethylene diamine, and mixtures thereof.

11. A shoe sole comprising the microcellular elastomer of any of claims 3 to 10.

12. A midsole comprising the microcellular elastomer of any of claims 3 to 10.

[19]中华人民共和国国家知识产权局

[51]Int. Cl⁷
C08G 18/48
C08G 18/12

[12]发明专利申请公开说明书

[21]申请号 99811410.3

[43]公开日 2001年10月31日

[11]公开号 CN 1320131A

[22]申请日 1999.7.27 [21]申请号 99811410.3
[30]优先权
[32]1998.9.25 [33]US [31]09/160,968
[86]国际申请 PCT/EP99/05375 1999.7.27
[87]国际公布 WO00/18817 英 2000.4.6
[85]进入国家阶段日期 2001.3.26
[71]申请人 拜尔安特卫普有限公司
地址 比利时安特卫普
[72]发明人 D·J·侯

[74]专利代理机构 中国专利代理(香港)有限公司
代理人 庞立志 郇 红

权利要求书2页 说明书11页 附图页数0页

[54]发明名称 制备微孔聚氨酯弹性体的方法

[57]摘要

本发明公开了微孔弹性体和制备它们的方法。该方法包括将树脂组分（"B"部分）与异氰酸酯终端的预聚物（"A"部分）反应。将适当比例的扩链剂预先反应到也包括高伯数、低不饱和度多元醇的"A"部分中是在避免与低劣的加工性或低等物理性能相关的问题的同时制备低密度（低于0.5g/cm）微孔弹性体的关键。该方法容易实施，和提供了更轻的、高质量聚氨酯产品，其中包括防护性运动设备、汽车工业的臂扶手或驾驶盘和鞋类的鞋底夹层或鞋底。

ISSN 1008-4274

知识产权出版社出版

权 利 要 求 书

1. 一种方法，其包括任选在发泡剂、表面活性剂和催化剂的存在下将树脂组分（“B”部分）与异氰酸酯终端的预聚物（“A”部分）反应以产生密度低于500kg/m^{3}的微孔聚氨酯弹性体；

其中树脂组分包括第一扩链剂和第一高伯数、低不饱和度多元醇的混合物；

其中预聚物通过将多异氰酸酯、可以与第一多元醇相同或不同的第二高伯数、低不饱和度多元醇和可以与第一扩链剂相同或不同的第二扩链剂反应来制备；和

其中反应到“A”部分中的第二扩链剂占总扩链剂的5－60当量百分数。

2. 权利要求1的方法，其中第二扩链剂占总扩链剂的10－40当量百分数。

3. 微孔聚氨酯弹性体，它包括以下组分的反应产物：

(a)包括以下物质的混合物的树脂组分（“B”部分）：

(i)第一高伯数、低不饱和度多元醇；

(ii)第一扩链剂；

(iii)任选存在的发泡剂、表面活性剂和催化剂；和

(b)包括以下组分的反应产物的异氰酸酯终端的预聚物（“A”部分）：

(i)多异氰酸酯；

(ii)第二高伯数、低不饱和度多元醇，它可以与第一多元醇相同或不同；和

(iii)第二扩链剂，它可以与第一扩链剂相同或不同；

其中反应到“A”部分中的第二扩链剂占总扩链剂的5－60当量百分数；和

其中弹性体具有低于500kg/m^{3}的密度。

4. 权利要求3的弹性体，它具有在20－400kg/m^{3}范围内的密度。

5. 权利要求3或4的弹性体，其中“B”部分包括聚合物多元醇。

6. 权利要求3、4或5的弹性体，其中发泡剂是水。

7. 权利要求3－6中任一项的弹性体，其中多异氰酸酯包括较多比例的4,4’-MDI和较少比例的碳二亚胺改性的MDI的混合物。

8. 权利要求 3－7 中任一项的弹性体，其中多元醇之一或两种均具有高于 75％的伯羟基端基含量和低于 0.007meq/g 的不饱和度水平.

9. 权利要求 3－8 中任一项的弹性体，其中第二扩链剂占总扩链剂的 10－40 当量百分数.

10. 权利要求 3－9 中任一项的弹性体，其中扩链剂之一或两种均选自乙二醇，丙二醇，二甘醇，二丙二醇，三甘醇，三丙二醇，乙二胺和它们的混合物.

11. 包括权利要求 3－10 中任一项的微孔弹性体的鞋底.

12. 包括权利要求 3－10 中任一项的微孔弹性体的鞋底夹层.

说　明　书

制备微孔聚氨酯弹性体的方法

本发明的领域

本发明涉及微孔聚氨酯弹性体和制备它们的方法．弹性体对于各种用途，最显著的是在汽车应用和鞋类中是很有价值的．

本发明的背景

微孔聚氨酯弹性体是众所周知的．它们具有细的、均匀分布的泡孔，以及低于固体脲烷弹性体而高于柔性聚氨酯泡沫的密度．微孔聚氨酯弹性体用于汽车部件（例如，保险杠和扶手），衬垫，振动阻尼应用和鞋类中．

尽管已经公开了制备微孔聚氨酯弹性体的许多方法，大多数方法归纳为两类：一步法和预聚物法．在一步法中，全部组分（多元醇，多异氰酸酯，发泡剂，表面活性剂，催化剂，扩链剂）在一步中混合和反应．相比而言，预聚物法将多异氰酸酯与多元醇进行预反应以制备“预聚物”（“A”部分），随后在第二步中与包括任何扩链剂的其余反应剂(“B”部分)结合以制备弹性体．如 U.S. 专利 No. 4,559,366 所说明的那样，通过使用多元醇与足够的多异氰酸酯反应产生的异氰酸酯终端的预聚物和游离多异氰酸酯的混合物能够有利地制备“准预聚物”．这种准预聚物普通用于提升“A”部分的可利用的 NCO 含量．

从异氰酸酯和多元醇-扩链剂混合物制备预聚物（“A”部分）也是已知的．例如，U.S. 专利 No. 5,658,959 教导了从 MDI，二丙二醇，聚丙氧基化/乙氧基化甘油，和聚丙氧基化/乙氧基化二醇制备异氰酸酯终端的预聚物（参见实施例 1）．参考多元醇具有至多 35wt% 的环氧乙烷含量，但未公开“封端”的度或伯羟基含量（参见第 5 栏，17－38 行）．该参考文献对多元醇的不饱和度也未说明．U.S. 专利 5,618,967 含有类似的公开内容．总之，这些参考文献既没有提出多元醇的不饱和度，也没有提出多元醇的伯羟基含量，而这些是很重要的．

U.S. 专利 No. 5,284,880 也提出了从异氰酸酯，多元醇和扩链剂（二丙二醇）制备的预聚物（例如参见 13 栏，30－45 行）．然而，该参考文献教导“A”部分多元醇必须是“主要含有仲羟基的聚醚”

（参见摘要；2栏，4－5行；和4栏，28－54行）．该参考文献对于低不饱和度多元醇的任何要求也未说明．

具有低水平不饱和度(<0.020meq/g)的多元醇一般对于聚氨酯和尤其对于微孔聚氨酯弹性体的益处是已知的．例如U.S.专利Nos.5,677,413和5,728,745叙述了从不饱和度低于0.010meq/g的多元醇制备的微孔聚氨酯．后一专利通过预聚物法（参见对比文献的实施例8和表6）或通过一步法（参见对比文献的实施例9－11和表8)制备弹性体．实施例8的预聚物是聚氧化丙二醇或三醇与4,4'-MDI的反应产物．不使用扩链剂制备预聚物．在实施例9－11中，使用高伯数、低不饱和度多元醇．参考文献教导了使用低不饱和度多元醇的几个优点，包括良好的回弹性，低压缩变定和减少的收缩率；这些优点对于鞋底是尤其重要的．

U.S.专利No.5,106,874教导了预聚物法和一步法从低不饱和度多元醇制备无孔弹性体．预聚物一般通过将聚氧化亚烷基多元醇与过量的多异氰酸酯反应来制备．该参考文献教导，扩链剂能够包括在预聚物中（7栏，49－52行）．然而，没有一个实施例包括反应到“A”部分中的扩链剂，以及没有制备微孔弹性体．

U.S.专利No.5,696,221教导了通过将预聚物与扩链剂反应来制备聚氨酯/脲弹性体．除了低不饱和度、聚氧化丙二醇以外，预聚物包括分子量低于400的二元醇．该参考文献没有公开微孔弹性体．

虽然在配方设计微孔聚氨酯弹性体中使用低不饱和多元醇时有广泛认可的优点，但与普通的一步法和预聚物法相关的一些问题得到保留．如在U.S.专利No.4,559,366中指出的那样，对于作为鞋底弹性体的普遍采用的原料的4,4'-二苯基甲烷二异氰酸酯(4,4'-MDI)不易于使用一步法，因为它不易于与其它反应剂混溶以及它在室温下固化（参见参考文献的第1栏）．

然而，预聚物方法也有缺点．配制高质量的、低密度弹性体，尤其密度低于0.5g/cm^{3}的那种是困难的．降低密度的明显方法是增加发泡剂（通常是水）的用量．然而，这会增加弹性体的脲含量，降低伸长率和降低柔性．添加多种扩链剂到“B”部分中可帮助在低密度下保持良好的硬度，但这会导致低劣的可加工性和早期相分离．如对比实施例8（下面）所示的那样，这种产物经常发生不希望的表面缺陷

和内部开裂.

虽然已知在“A”部分中包括一些扩链剂，但很少或不知道这样做在制备以低不饱和度多元醇、尤其具有高含量的伯羟基的那些为基础的微孔弹性体中的益处.

总之，工业上将会从制备微孔聚氨酯弹性体的更好方式中受益.优选方法使用现在已知的低不饱和度多元醇以赋予聚氨酯显著的物理性能优点.有价值的方法将是容易实施的，还克服了尤其在配制低密度弹性体中的普通一步法和预聚物法的缺点.

本发明的概述

本发明是能使微孔弹性体的配制料获得低于 0.5g/cm³ 的密度而无需以牺牲良好的加工范围或优异的弹性体性能为代价的突破性方法.该方法包括将树脂组分（“B”部分）与异氰酸酯终端的预聚物（“A”部分）任选在发泡剂、表面活性剂和催化剂的存在下反应.树脂组分包括第一扩链剂和第一高伯数、低不饱和度多元醇.然而，关键组分是预聚物，它是通过将多异氰酸酯，第二高伯数、低不饱和度多元醇和第二扩链剂反应制得的.反应到“A”部分中的第二扩链剂占总扩链剂的大约 5 到大约 60 当量百分数.

令人惊奇的发现，使适当比例的扩链剂组分预反应到也包括高伯数、低不饱和度多元醇作为预聚物的一部分的“A”部分中是制备低密度（低于 0.5g/cm³）微孔弹性体，同时避免与低劣的加工性或低等物理性能有关的问题的关键所在.该方法容易实施，并提供了更轻的、高质量的聚氨酯产品，其中包括防护性运动设备，汽车工业的臂扶手或驾驶盘，以及鞋类的鞋底夹层或鞋底.

本发明的详细描述

在本发明的方法中，树脂组分（“B”部分）包括第一高伯数、低不饱和度多元醇和扩链剂.

用于本发明方法的多元醇通过环醚的开环聚合反应制备，并包括环氧化物聚合物、氧杂环丁烷聚合物、四氢呋喃聚合物等.多元醇能够通过任何理想的方法制得；然而，终产物必须具有低不饱和度和高含量的伯羟基.由聚合环氧化物，尤其环氧丙烷和/或环氧乙烷制备的聚醚多元醇是优选的.尤其优选的是用氧化乙烯基封端或终端的环氧丙烷型多元醇.

多元醇有高含量的伯羟基端基．这类多元醇通常通过用氧化乙烯单元终端或封端聚氧化丙烯多元醇的端部．“高伯数”是指具有至少大约 50％的伯羟基的多元醇．更优选的是，多元醇具有至少大约 65％的伯羟基，最优选的是具有至少大约 75％伯羟基的多元醇．高伯羟基含量是重要的；因为下面的对比实施例 6 显示，当在本发明方法中使用低伯数多元醇时得到了低劣的弹性体．

多元醇也具有低不饱和度．“低不饱和度”是指根据标准方法，如 ASTM D-2849-69，“Testing of Urethane Foam Polyol Raw Material”测量的低于大约 0.02meq/g 的不饱和度．优选的多元醇具有低于大约 0.01meq/g 的不饱和度；最优选的是不饱和度低于大约 0.007meq/g 的多元醇．具有很低不饱和度水平的多元醇可方便地由例如在 U.S. 专利 Nos. 5,470,813 和 5,482,908 所述的双金属氰化物催化法制备，该教导在这里引入作为参考．

多元醇优选具有低于大约 3 的平均羟基官能度．更优选的范围是大约 1.8－大约 3.0．另外，多元醇优选具有在大约 500－大约 50,000 范围内的数均分子量．更优选的范围是在大约 1000－大约 6000；最优选是在大约 2000－大约 6000 的范围内．

多元醇优选具有至少大约 5wt％，更优选大约 10－20wt％的氧化乙烯含量，它能存在于内部，顶端或末端．优选的是，氧化乙烯含量的大多数是位于多元醇的末端以便提供理想的高含量的伯羟基．

高伯数、低不饱和度多元醇一般是“B”部分的主要组分．一般，它占树脂组分的至少大约 40wt％．优选范围是树脂组分的大约 45－大约 90wt％，更优选大约 50－70wt％．

树脂组分也包括扩链剂．有用的扩链剂具有至少两个活性氢，和包括低分子量二元醇，二胺，氨基醇，二硫醇，或类似物．优选的是，扩链剂具有低于大约 400，更优选低于大约 300 的数均分子量．二元醇是优选的扩链剂．适合的扩链剂例如包括乙二醇，丙二醇，2-甲基-1,3-丙二醇，1,4-丁二醇，二甘醇，二丙二醇，三甘醇，三丙二醇，新戊二醇，环己烷二甲醇，1,6-己二醇，乙二胺，乙烷二硫醇等，以及它们的混合物．尤其优选的是二丙二醇，乙二醇和 1,4-丁二醇．如果需要，能够包括较少比例的具有 3 或 3 个以上活性氢的扩链剂（例如甘油）．

扩链剂是较少的“B”部分组分．典型地，它占树脂组分的低于大约 30wt%．优选的范围是树脂组分的大约 1－大约 20wt%，更优选大约 3－大约 10wt%．

树脂组分任选包括可以是或不是低不饱和度或高伯数多元醇的其它多元醇．优选的是，树脂组分包括聚合物多元醇．适合的聚合物多元醇包括通过乙烯基单体在基料多元醇中的就地聚合以得到在基料多元醇中聚合物颗粒的稳定分散体所制备的众所周知的那些，如苯乙烯-丙烯腈（SAN）聚合物多元醇．其它的适合的聚合物多元醇包括 PIPA 和 PHD 多元醇，它们是－象 SAN 聚合物多元醇一样－可以商购的．这些聚合物多元醇具有一般在大约 5－大约 50wt%的聚合物固体含量．当聚合物多元醇被包括时，优选使用 5－大约 45wt%范围内的量，基于树脂组分的总量．

在本发明的方法中异氰酸酯终端的预聚物（“A”部分）与树脂组分（“B”部分）反应．预聚物是多异氰酸酯、第二高伯数、低不饱和度多元醇和第二扩链剂的反应产物．

多异氰酸酯是含有至少两个游离 NCO 基的芳族、脂族或环脂族异氰酸酯．适合的多异氰酸酯包括二苯基甲烷二异氰酸酯（MDI），聚合 MDI，MDI 变型体，甲苯二异氰酸酯，六亚甲基二异氰酸酯，异佛尔酮二异氰酸酯等，以及它们的混合物．优选的多异氰酸酯是 4,4’-MDI，其它含有较高比例的 4,4’-MDI 异构体的 MDI 共混物，以及通过将 MDI 与其本身另一组分反应以便将碳二亚胺、脲基甲酸酯、脲、脲烷、缩二脲或其它连接基引入到结构中所制备的改性 MDI（MDI 变异体）．尤其优选的是 4,4’-MDI，碳二亚胺改性的 MDI 和它们的混合物．所使用的多异氰酸酯的量优选是得到具有游离 NCO 量在大约 15－大约 30wt%、更优选大约 20－大约 28wt%范围内的 NCO-终端的预聚物或准预聚物所需的量．

预聚物包括第二高伯数、低不饱和度多元醇，它与第一高伯数、低不饱和度多元醇可以是相同或不同的．然而，第二多元醇具有与第一多元醇相同的总特性，即低不饱和度（低于 0.02meq/g）和高含量（至少大约 50%）的伯羟基．高伯数、低不饱和度多元醇是次要的“A”部分组分．异氰酸酯终端的预聚物优选占预聚物组分的大约 1－大约 10wt%的；更优选的范围是大约 2－大约 8wt%．

预聚物还包括扩链剂．该扩链剂（“第二”扩链剂）可以是相同或不同于在树脂组分中所使用的扩链剂（“第一”扩链剂）．另外，第二扩链剂符合第一扩链剂的上述条件．反应到“A”部分中的第二扩链剂占总扩链剂的大约 5－大约 60 当量百分数．优选的是，第二扩链剂占总扩链剂的大约 10－大约 40 当量百分数；最优选的范围是大约 15－大约 35 当量百分数．

用于制备预聚物的扩链剂的量是重要的．如果低于大约 5 当量百分数，会导致泡沫分裂、表面缺陷和其它问题（参见对比实施例 8）．另一方面，如果总扩链剂的大约 60 当量百分数以上存在于“A”部分中，会产生过剩的热量，这能导致预聚物不想要的凝胶化．

虽然大多数预聚物是多异氰酸酯和多元醇的简单反应产物，但本发明将扩链剂引入到了预聚物中．发明人惊奇地发现，将总扩链剂的 5－60 当量百分数预先反应到“A”部分中，并结合使用高伯数、低不饱和度多元醇是制备低密度（低于 0.5g/cm^3）微孔弹性体同时避免与低劣加工性或低等物理性能相关的问题的关键．该简单步骤对于提供更轻的、高质量的聚氨酯产物，尤其鞋类的鞋底夹层或鞋底是关键性的．

预聚物一般通过将第二多元醇、第二扩链剂和多异氰酸酯以任何理想的次序混合，和以有效产生异氰酸酯终端的预聚物的温度和时间加热混合物来制备的．通常，优选在引入第二扩链剂之前将多异氰酸酯和高伯数、低不饱和度多元醇一起短时间反应．然后继续加热直到预聚物达到理想含量的游离 NCO 基为止．在另一优选的方式，在预聚物形成的反应的开始阶段包括了全部或部分的第二扩链剂．

在预聚物制备之后，使用普通工艺混合树脂组分以制备微孔弹性体．树脂组分是第一低不饱和度多元醇、第一扩链剂和其它任选的组分如发泡剂、表面活性剂、催化剂等的充分共混的混合物．弹性体可以通过手工铸塑或机加工制备．结合“A”和“B”部分，快速混合，以及注塑或倾倒在开放或封闭的模具中．这里所述的配制料非常适合于与用于通过闭模技术制造鞋底夹层和鞋底的商购设备（如 Gusbi 模塑机）一起使用．

优选的是，本发明的方法在发泡剂的存在下实施．适合的发泡剂是在配制微孔聚氨酯弹性体的技术领域中众所周知的那些．它们包括

“物理”发泡剂，如低沸点的卤化碳（例如，CFC、HCFC、二氯甲烷）或烃类（如丁烷、戊烷），惰性气体（例如氮气、氩气、二氧化碳），或类似物，以及“反应活性”发泡剂，如可与 NCO 基反应释放气体的水和其它活性氢化合物．能够使用发泡剂的混合物．水是尤其优选的发泡剂．发泡剂以产生密度低于 0.5g/cm^3 的微孔弹性体所需的量使用．优选的是，所得到的弹性体具有大约 0.02－0.4g/cm^3范围内的密度；最优选的是在大约 0.1－大约 0.3g/cm^3范围内．

本方法任选包括其它普通聚氨酯泡沫组分，如表面活性剂、发泡催化剂、脲烷形成催化剂、颜料、UV 稳定剂、交联剂、抗氧化剂、其它多元醇和/或其它添加剂．这些任选的组分在将它与“A”部分反应以制备弹性体之前优选与树脂组分彻底混合．

本发明的方法提供了弹性体加工的优点．适量的扩链剂“移入”到“A”部分组分中得到了在弹性体加工过程中对反应活性和可流动能力的改进控制，因为在弹性体的配制之前总反应的大部分已发生了．该方法也提供了宽的加工范围．如以下实施例所证实的那样，能够在宽的温度范围内（40－60℃）和宽的指数范围内（95－105）制备优异的产物，而且脱模时间是短的（<7 分钟）．

该方法也提供了物理性能优点．在过去，很难在避免产品质量问题的同时制备密度低于 0.5g/cm^3的（尤其密度低于 0.3g/cm^3的那种）微孔弹性体．使用本发明方法制备的微孔弹性体具有优异的拉伸和撕裂强度，良好的表面质量，以及没有内部开裂．如下面实施例所表明的那样，本发明的方法使得可能容易地配方设计出密度低至大约 0.26g/cm^3的优异弹性体．

以下的实施例仅仅说明本发明．本技术领域的那些技术人员将会认识到在本发明的实质和权利要求范围内的许多变型．

实施例 1－5 和对比实施例 6

使用 Gusbi 机器在 35℃下由下面所述的“A”和“B”部分组分的反应注塑混合物来模塑 10mm 微孔弹性体平板．模具温度是在 40－60℃范围内．产物在低于 1 分钟内变得无粘性．物理性能在表 1 给出．

如表中所示，密度低于 0.27g/cm^3和各项性能有优异平衡的微孔弹性体可从本发明的方法获得．在本发明的一个实施例中，“A”部分包括扩链剂（二丙二醇）和高伯数、低不饱和度多元醇．对比实施

例 6 证实了使用“高伯数”多元醇的重要性。低不饱和度单独不足以得到这种低密度的优质产物。

配方

树脂组分（“B”部分）	pbw
低不饱和度多元醇（见表 1）	58
聚合物多元醇[1]	35
水	1.1
乙二醇	5.2
Dabco EG 催化剂[2]	0.2
X-8154 催化剂[2]	1.0
BL-17 催化剂[2]	0.2
T-120 催化剂[2]	0.02
DC-193 表面活性剂[3]	0.25
LK-221 乳化剂[2]	0.75
颜料（例如碳黑或 TiO）	1.2
B-75 稳定剂[4]	1.0
预聚物（“A”部分；24wt% NCO）	
4,4’-MDI	80
碳二亚胺-改性的 MDI	8
低不饱和度多元醇（见表 1）	5
二丙二醇	7

---

[1] SAN 型，43wt% 固体含量，羟基数 20mg KOH/g

[2] Air Products 的产品；[3] Dow Corning 的产品；[4] Ciba-Geigy 的产品。

表 1 微孔聚氨酯弹性体

实施例	1	2	3	4	5	6
树脂多元醇	A-4220	A-4220	A-4220	A-2220	A-4220	A-3201
预聚物多元醇	A-4220	A-4220	A-4220	A-2220	A-2220	A-3201
A/B 部分(w/w)	0.53	0.55	0.58	0.55	0.55	0.55
指数(NCO/OH)	0.95	1.00	1.05	1.00	1.00	1.00
物理性能						
密度(g/cm^3)	0.265	0.265	0.265	0.265	0.265	0.265
硬度(Asker C)	61	62	62	60	60	58
拉伸强度(kg/cm^2)	19.4	20.8	23.2	16.4	19.2	*
伸长率(%)	307	255	296	319	324	*
剖层撕裂(kg/cm, 10mm)	2.3	2.6	2.6	1.9	2.1	*

A-4220 是 Accuflex 4220 多元醇，具有 Mn=4000、大约 20wt% 的氧化乙烯含量（5% 内部，15% 端部），以及大约 85% 的伯羟基含量的聚氧化丙烯二醇；A-2220 是 Accuflex 2220 多元醇，具有 Mn=2000、大约 20wt% 的氧化乙烯含量（5% 内部，15% 端部），以及大约 85% 的伯羟基含量的聚氧化丙烯二醇；

A-3201 是 Accuflex3201 多元醇，具有 Mn=3000，大约 10wt％的内部氧化乙烯含量的聚氧化丙烯二醇；全部是 ARCO Chemical 的产品.

*样品裂开和不能测试.

实施例 7

按照实施例 1－5 的工序，只是预聚物使用 52 份的 4,4'-MDI，4 份的二丙二醇和 3 份的 Accuflex4220 多元醇制备。

所得到的鞋底夹层是优异的，其能够在 40－60℃的宽温度范围内容易被模塑加工而成。物理性能：密度：0.26g/cm^3；Asker C 硬度：60－65；剖层撕裂强度：2.0kg/cm；拉伸强度：19kg/cm^2。脱模时间低于 7 分钟，以及没有明显的表层剥离或内部开裂。

对比实施例 8

在本实施例中，所使用的全部扩链剂被包括在树脂组分内（“B”部分）。

按照实施例 7 的工序，有以下改变：树脂共混物含 1.5 份的水和 12.5 份的乙二醇。预聚物使用 81 份的 4,4'-MDI 和 46 份的 Accuflex4220 多元醇制备，不使用扩链剂。

所得到的鞋底夹层是差的。物理性能：密度：0.26g/cm^3；Asker C 硬度：60－65；剖层撕裂强度：1.6kg/cm；拉伸强度：17kg/cm^2。脱模时间是 7 分钟或更多，许多试样具有差的表面质量，这在脱模时更加明显。此外，许多部分有内部开裂。

前述实施例仅作为例证；下面的权利要求书定义本发明的范围。

HKP0120341

PROCESS FOR MAKING MICROCELLULAR POLYURETHANE ELASTOMERS

Mircrocellular elastomers and a process for making them are disclosed. The process comprises reacting a resin component ("B" side) with an isocyanate-terminated prepolymer ("A" side). Pre-reacting the right proportion of chain extender into an "A" side that also includes a high-primary, low-unsaturation polyol is the key to making low-density (less than 0.5 g/cm^3) microcellular elastomers while avoiding problems with poor processing or inferior physical properties. The process is easy to practice, and provides lighter, high-quality polyurethane products, including protective sports equipment, arm rests or steering wheels for the auto industry, and midsoles or shoe soles for footwear.