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(12) (19) (CA) **Demande-Application**

(21) (A1) **2,303,381**
(86) 1998/09/29
(87) 1999/04/08

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(51) Int.Cl.$^7$ C08G 18/10, C08G 18/08
(30) 1997/10/01 (60/060,718) US

# (54) EXTRUSION REACTIVE DE POLYMERES LIQUIDES POUVANT ETRE FACONNES SUR MESURE

# (54) REACTIVE EXTRUSION OF TAILORED LIQUID POLYMERS (TLPS)

(57) L'invention concerne un procédé servant à préparer des polymères de polyuréthanne par extrusion d'un polyuréthanne liquide coulant (TLP). On prépare ce TLP à partir d'un polyisocyanate et d'un polyol à basse température. On peut produire des polymères de polyuréthanne élastomères à partir du TLP au moyen d'un processus d'extrusion réactive. On peut réitérer le traitement de ces polymères de polyuréthanne élastomères obtenus, un certain nombre de fois sous forme de fusion (traitement en fusion) et on peut ensuite façonner le polymère en différentes formes utiles.

(57) The present invention is a process for preparing polyurethane polymers by extruding a free flowing liquid polyurethane (TLP). A TLP is prepared from a polyisocyanate and a polyol at low temperature. Elastomeric polyurethane polymers can be obtained from the TLP by a reactive extrusion process. Elastomeric polyurethane polymers thus obtained can be re-processed as a melt (melt processed) a number of times, and the polymer formed into various useful forms.

**PCT**

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

# INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

**(51) International Patent Classification $^6$ :**
**C08G 18/10, 18/08**

**A1**

**(11) International Publication Number:** **WO 99/16806**

**(43) International Publication Date:** 8 April 1999 (08.04.99)

**(21) International Application Number:** PCT/US98/20351

**(22) International Filing Date:** 29 September 1998 (29.09.98)

**(30) Priority Data:**
60/060,718 1 October 1997 (01.10.97) US

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**(81) Designated States:** AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, 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, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, 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: REACTIVE EXTRUSION OF TAILORED LIQUID POLYMERS (TLPS)

**(57) Abstract**

The present invention is a process for preparing polyurethane polymers by extruding a free flowing liquid polyurethane (TLP). A TLP is prepared from a polyisocyanate and a polyol at low temperature. Elastomeric polyurethane polymers can be obtained from the TLP by a reactive extrusion process. Elastomeric polyurethane polymers thus obtained can be re-processed as a melt (melt processed) a number of times, and the polymer formed into various useful forms.

# REACTIVE EXTRUSION OF TAILORED LIQUID POLYMERS (TLP'S)

The present invention relates to polyurethane polymers. The present invention particularly relates to polyurethane polymers and to a process for preparing same.

It is known to prepare polyurethane polymers from polyols, polyisocyanates and other additives by combining an isocyanate "A-side" mixture with a polyol "B-side" mixture. Isocyanates and polyols are conventionally combined to make polyurethanes using what is known in the art of making polyurethane polymers as "A/B" polyurethane chemistry. Polyurethane polymers are useful as flexible foams, rigid foams, elastomers, coating resins, adhesives, sealants, fibers, and films.

Conventional preparation of polyurethane polymer materials using traditional "A/B" chemistry requires that a manufacturer of polyurethane polymer products prepare the polymer on site. This can present problems for certain manufacturers of polyurethane products.

Extrusion of thermoplastic polymers such as polystyrene and acrylate polymers such as poly(methyl methacrylate) is a well-known process. See, for example, each of the following, each with respect to the teachings on extrusion processes: James M. McKelvey, Plastics Processing, John Wiley & Sons, New York, 1962; A. S. Haisser, "Extrusion", in Modern Plastics Encyclopedia 1982-1983, Vol. 59, No. 10A, McGraw-Hill, New York, 1982; Paul N. Richardson, Introduction to Extrusion, John Wiley & Sons, New York, 1974. Extrusion is a fabrication process whereby polymeric materials are shaped or re-cast into useable, salable pieces of polymeric materials. Typically, in an extrusion process a polymer is pushed continuously along a screw while being melted and compacted in regions of high pressure and temperature. The polymer is finally forced through a die which gives the polymer its final shape. Polymers having shapes which include tubing, hose, sheets, and films, for example, and can be made in an extrusion process.

It would be desirable in the art of preparing polyurethane polymers to prepare such polymers from materials that have low viscosity and little chain extension. It would also be desirable in the art of preparing polyurethane polymers to obtain foams, films, gels, adhesives, and hard elastomers directly from an extruder by an extrusion process.

In one aspect, the present invention is a process for preparing, from isocyanate-terminated prepolymers, melt-processable elastomeric polymers comprising a urethane linkage, wherein the polymers are obtained by a reactive extrusion process comprising the steps: (a) feeding a liquid prepolymer to an extruder device; (b) passing the prepolymer of step (a) through the extruder while heating the prepolymer; and (c) extruding an elastomeric polymer.

In another aspect the present invention is a polyurethane polymer obtained by preparing, from isocyanate-terminated prepolymers, melt-processable elastomeric polymers comprising a urethane linkage, wherein the polymers are obtained by a reactive extrusion process comprising the steps: (a) feeding a liquid prepolymer to an extruder device; (b) passing the prepolymer of step (a) through the extruder while heating the prepolymer; and (c) extruding an elastomeric polymer.

Polyurethane polymers described herein can be prepared from tailored liquid polymer (TLP) prepolymers in either the absence or presence of a polyurethane catalyst. TLPs can be crosslinked in a reactive extrusion process wherein the TLP is fed to an extruder and processed as a liquid, is crosslinked to form the polymer as it is being forced through the screw cavity. Polymers of the present invention are melt-processable, that is polymers that can be processed above the $T_g$ of the polymer material. For the purposes of the present application, melt-processable polymers of the present invention can be formed from reactants, in the substantial absence of a solvent, at a temperature greater than the Tg of the product obtained, and the polymer product subsequently processed as a melt. Melt processable polymers can be heated above the Tg of the polymer and shaped, molded or otherwise physically altered as a polymer melt.

The term “polyurethane”, as used herein, is not limited to those polymers which include only urethane or polyurethane linkages. It is well understood by those of ordinary skill in the art of preparing polyurethanes that the polyurethane polymers also include allophanate, biuret, carbodiimide, oxazolinyl, isocyanurate, uretidinedione, urea, and other linkages in addition to urethane linkages.

In one embodiment, melt processable polymers of the present invention can be obtained by reactive extrusion of a TLP. A reactive extrusion process is similar to a conventional extrusion process, except that the material fed into the extruder is chemically reacted and physically modified inside of the extruder. In a conventional extrusion process no chemical reaction is carried out in the extruder. Typically, a pre-formed polymeric material is physically modified by softening and re-shaping a polymer into a particular form.

TLPs are free flowing liquid oligomeric polyurethane materials prepared by reaction of a polyisocyanate with a polyol. The reaction between the polyisocyanate and the polyol is carried out at low temperature and in the absence of catalyst. The TLP thus obtained has low viscosity and has very little chain extension. The preparation of TLPs is known and described in World Patent publication number W09634904-A1. By low temperature, it is meant that a TLP material can be prepared at a temperature less than about 150°C. Preferably a TLP is prepared at a temperature of from 20°C to 125°C. More preferably, a TLP is prepared at a temperature of from 25°C to 115°C, and most preferably from a temperature of from 25°C to 100°C.

A TLP of the present invention can have any molecular weight, so long as the TLP is a free flowing liquid prepolymer material. A TLP suitable for use in the practice of the present invention can be a single TLP prepolymer or a mixture of at least two prepolymers. Whether a single component or a mixture, a TLP of the present invention optionally has a functionality in the range of from 2 to 6. In a preferred embodiment, one prepolymer of a prepolymer mixture can have functionality of about 2 with a molecular weight of less than about 10,000 and the other prepolymer can have multi-functionality with molecular weight of less than about 12,000. More preferred is a prepolymer mixture wherein at least one prepolymer has functionality about 2 and a molecular weight of from 2000 to 10,000, and a second prepolymer of the mixture has a functionality of about six (6) and a molecular weight of from 3,000 to 12,000. It is preferred in the practice of the present invention that the TLP has functionality and molecular weight such that it is a free flowing liquid at less than about 50°C, and more preferably, the TLP has a molecular weight and functionality such that it is a free flowing liquid at less than about 20°C. Prepolymer components used in the mixture herein can be combined in any ratio that will provide the average prepolymer functionality suitable for the practice of the present invention. Prepolymers having low monomer content are preferred in the practice of the present invention. Monomer content of less than 20 percent, preferably less than 15 percent and more preferably less than 10 percent is desirable in the practice of the present invention.

A TLP can be reactively extruded, and an elastomeric polyurethane polymer obtained, by feeding the TLP into an extruder and processing the TLP at a screw speed of from 10 to 200 rpm. The TLP can be processed in the extruder at a temperature of from 25°C to 250°C. Preferably the TLP is passed through the extruder at a temperature of from 50°C to 160°C, at a screw speed of from 50 rpm to 200 rpm. More preferably, a TLP is passed through an extruder at a temperature of from 60°C to 140°C, at a screw speed of from 100 to 150 rpm.

A polyisocyanate suitable for use in the practice of the present invention can be any polyisocyanate known to be useful in the preparation of polyurethane foams. A suitable polyisocyanate can be either aliphatic or aromatic. Aromatic polyisocyanates suitable for use herein include: phenyl diisocyanate; 2,4-toluene diisocyanate; 2,6-toluene diisocyanate; ditoluene diisocyanate; naphthalene 1,5-diisocyanate; 2,4'- and/or 4,4'-diphenylmethane diisocyanate (MDI); polymethylene polyphenylenepolyisocyanates (polymeric MDI); like compounds, and mixtures thereof. Suitable aliphatic polyisocyanates include: the hydrogenated derivatives of suitable aromatic polyisocyanates such as 1,6-hexamethylene diisocyanate; isophorone diisocyanate; 1,4-cyclohexyl diisocyanate; like compounds and mixtures thereof. Also suitable for use in the practice of the present invention are prepolymers prepared from polyisocyanates and polyols described herein, as is known in the art. Preferred in the practice of the present invention is TDI.

TLPs can be prepared by reaction of polyisocyanates with polyols, including lower molecular weight diols, triols, and can also be prepared using multivalent active hydrogen compounds such as di- and tri-amines and di- and tri-thiols. Individual examples are aromatic polyisocyanates containing urethane groups, preferably having NCO contents of from 0 to 40 weight percent, more preferably 1 to 35 weight percent, obtained by reaction of diisocyanates and/or polyisocyanates with, for example, lower molecular weight diols, triols, oxyalkylene glycols, dioxyalkylene glycols or polyoxyalkylene glycols.

A "B"-side formulation of the present invention can include an active hydrogen containing compound, capable of reacting with isocyanate functionality, in addition to other optional components. Active hydrogen containing compounds, as the term is used herein, are compounds having functionality that is reactive with Zerewitinoff reagent. Generally, active hydrogen-containing compounds include alcohols, amines, and mercaptans, for example. Polyols are active hydrogen containing compounds suitable for use in the practice of the present invention. Representatives of polyols suitable for use with the process of the present invention are generally known and are described in such publications as High Polymers, Vol. XVI, "Polyurethanes, Chemistry and Technology" by Saunders and Frisch, Interscience Publishers, New York, Vol. I, pp. 32-42, 44-54 (1962) and Vol. II, pp. 5-6,198-199 (1964); Organic Polymer Chemistry by K. J. Saunders, Chapman and Hall, London, pp. 323-325 (1973); and Developments in Polyurethanes, Vol. I, J. M. Buist, ed., Applied Science Publishers, pp. 1-76 (1978). Examples of such materials include those selected from the following classes of compositions, alone or in admixture: (a) alkylene oxide adducts of polyhydroxyalkanes; (b) alkylene oxide adducts of non-reducing sugars and sugar derivatives; (c) alkylene oxide adducts of polyphenols; and (d) polyester polyols. Also preferred are poly(oxypropylene) glycols, triols, tetrols and hexols and any of these that are capped with ethylene oxide. These polyols also include poly(oxypropyleneoxyethylene)polyols.

Catalysts are optional in the practice of the present invention, but preferably are included. Catalysts suitable for use in the practice of the present invention include any trimerization catalysts known to those skilled in the art of preparing polyurethane polymers. A trimerization catalyst can be included in the formulation at from 0.01 to 1.0 percent by weight of the mixture (wt percent), preferably from 0.25 to 1.0 wt percent, more preferably from 0.25 to 0.75 wt percent, and most preferably from 0.25 to0.5 wt percent.

The present invention includes a chain extender. Chain extenders useful in the practice of the present invention are preferably liquid at room temperature, and can have a molecular weight of less than or equal to about 8,000. Preferably the chain extender has a molecular weight of from 50 to 8,000. Most preferably, the chain extender has a molecular weight of from 50 to 600. Chain extenders useful in the practice of the present invention have hydroxyl functionality. More preferably, chain extenders useful herein are diols. Diol chain extenders useful herein most preferably have primary hydroxyl functionality. Preferred chain extenders include, but are not limited to, ethylene glycol; diethylene glycol; diols derived from polyethylene oxides of molecular weight 200, 400, or 600; ethylene oxide-capped polypropylene oxide diols having a molecular weight of from 400 to 4000. A chain extender of the present invention should be included such that the isocyanate/hydroxyl ratio is in the range of from 1.00 to 100; preferably in the range of from 1.00 to 10.0; and more preferably in the range of from 1.50 to 2.00.

TLPs can be blended with other components. For example TLPs can be blended with other polymers and extruded to give a co-polymer product. TLPs can be blended with, for example, polyacrylates, polystyrenes, polyacrylonitriles. TLPs can also be blended with standard polyurethane prepolymers, MDI, or other polyols.

The present invention can include other optional components. For example, the present invention optionally includes a filler material. Conventional fillers such as milled glass, calcium carbonate, ATH, talc, bentonite clays, antimony trioxide, kaolin, fly ash, or other known fillers can be used in the practice of the present invention. A polyurethane-forming composition of the present invention can optionally include: surfactants; fire retardants; pigments; anti-static agents; reinforcing fibers; antioxidants; preservatives; water scavengers; acid scavengers.

In another embodiment, the present invention is a process for obtaining a melt processable polymer by reactive extrusion in a first stage, and in a second stage or in subsequent stages, melt-processing the polymer thus obtained to form a polymer that can be used in various applications. A polymer obtained from the first can be repeatedly re-processed as in the second stage without detrimental effect on the polymer obtained from the first stage. In a second or subsequent re-processing stage of the present invention, a polymer can be passed through an extruder at a temperature of from 100°C to 280°C, at a screw speed of from 5 to 50 rpm. Preferably the screw speed is from 10 to 50 rpm, and the temperature of the extruder is from 150°C to

280°C. Most preferably, the extruder screw speed is from 20 to 40 rpm, and the temperature of the extruder heated zone is in the range of from 180°C to 270°C.

Polyurethane elastomeric polymers obtained in the practice of the present invention can be useful in a variety of applications, including use as foams, films, gels, adhesives, non-woven fibers and hard elastomers. Elastomeric polymers obtained according to the practice of the present invention can demonstrate elongation of from 50 percent to 1000 percent.

## EXAMPLES

The following examples were merely illustrative of the present invention. They were not intended to - nor do they - represent the entire scope of the invention claimed herein.

Example 1

A 2000 equivalent weight polyol prepared from sorbitol and a 60:40 mixture of ethylene oxide and propylene oxide and toluene diisocyanate were combined to prepare a TLP. The TLP was fed to an extruder and extruded at zone temperature settings of 150, 165, 245, and 245°C and at a rate of 35 rpm to yield a polymeric material.

Example 2

A blend prepared by combining 100 parts of the TLP of Example 1 and 25 parts of a HEMA modified TLP was fed to an extruder and extruded at zone temperature settings of 150, 165, 195, and 225°C at a rate of 35 rpm to yield a polymeric material.

Example 3

The TLP of Example 1 was fed into an extruder and extruded with extruder heating zone temperatures of 150, 165, 225, and 225°C at 35 rpm to give a sticky gelled polymer.

Example 4

The TLP of Example 1 was fed into an extruder and extruded with extruder heating zone temperatures of 150, 165, 225, and 225°C at 35 rpm into a container of stirred water. The extruded material formed a foamed soft polymer which separated from the water.

Example 5

A blend of nominally 2 and nominally 6 functional TLP prepolymers, wherein the weight average functionality of the blend was greater than 2 but less than 3, incorporating 0.5 percent by weight trimerization catalyst was fed into the extruder and extruded at zone temperatures of 80, 110, 80 and 70 °C respectively at a screw speed of 150 rpm and yielded an elastomeric polymer material.

Example 6

A blend of nominally 2 and nominally 3 functional TLP prepolymers, wherein the weight average functionality of the blend was greater than 2 but less than 3, incorporating 0.75 percent by weight trimerization catalyst was fed into the extruder and extruded at zone temperatures of 80, 110, 80 and 70 °C respectively at a screw speed of 100 rpm and yielded an elastomeric polymer material.

Example 7

A blend of nominally 2 and nominally 6 functional TLP prepolymers, wherein the weight average functionality of the blend was greater than 2 but less than 3, incorporating 1.0 percent by weight of diethylene glycol and 0.5 percent by weight trimerization catalyst was fed into the extruder and extruded at zone temperatures of 80, 110, 80 and 70 °C respectively at a screw speed of 150 rpm and yielded an elastomeric polymer material.

Example 8

A blend containing a nominally 2 functional TLP prepolymer, 1.0 percent by weight of diethylene glycol and 0.5 percent by weight trimerization catalyst was fed into the extruder and extruded at zone temperatures of 80, 110, 80 and 70 °C respectively at a screw speed of 150 rpm and yielded an elastomeric polymer material.

Example 9

A blend of nominally 2 and nominally 6 functional TLP prepolymers, wherein the weight average functionality of the blend was greater than 2 but less than 3, incorporating 2.0 percent by weight trimerization catalyst was fed into the extruder and extruded at zone temperatures of 90, 110, 110, 140 and 120 °C respectively at a screw speed of 20-40 rpm and yielded an elastomeric polymer material.

Example 10

The polymer derived from example 7 was fed into the extruder hopper in the form of granules/chips/pellets and extruded at zone temperatures of 240, 260, 260, 250 °C at a screw speed of 20-40 rpm and yielded elastomeric polymer.

Example 11

The polymer derived from example 8 was fed into the extruder hopper in the form of granules/chips/pellets and extruded at zone temperatures of 240, 240, 240, 200 °C at a screw speed of 20-40 rpm and yielded elastomeric polymer.

Example 12

The polymer derived from example 9 was fed into the extruder hopper in the form of granules/chips/pellets and extruded at zone temperatures of 80, 110, 120, 140 and 120°C at a screw speed of 20-40 rpm and yielded elastomeric polymer.

1. A process for preparing, from isocyanate-terminated prepolymers, melt-processable elastomeric polymers comprising a urethane linkage, wherein the polymers are obtained by a reactive extrusion process comprising the steps:
(a) feeding a liquid prepolymer and a trimerization catalyst to an extruder device wherein the prepolymer has an isocyanate index of at least 1.1;
(b) passing the prepolymer and catalyst of step (a) through the extruder while heating and,
(c) extruding an elastomeric polymer.

2. The process of Claim 1 wherein a chain extender that is a liquid at room temperature having a hydroxyl functionality and a molecular weight of less than or equal to about 8,000 is fed into the extruder with the prepolymer and and trimerzation catalyst.

3. The process of Claim 2 wherein the prepolymer is heated in the range of from 25°C to 250°.

4. The process of Claim 3 wherein the prepolymer is heated in the range of from 50°C to 160°.

5. The process of Claim 4 wherein the prepolymer is heated in the range of from 60°C to 140°.

6. The process of any of the preceding claims wherein the prepolymer is fed through the extruder at a screw speed of from 10 to 200 rpm.

7. The process of Claim 6 wherein the prepolymer is fed through the extruder at a screw speed of from 50 to 200 rpm.

8. The process of Claim 7 wherein the prepolymer is fed through the extruder at a screw speed of from 100 to 150 rpm.

9. The process of any one of the preceding claims wherein the elastomeric polymer obtained is re-extruded at or above the softening point of the polymer.

10. The process of Claim 9 wherein the polymer is re-extruded at a temperature of from 100°C to 280°C and at a screw speed of from 5 to 50 rpm.

11. The process of Claim 10 wherein the polymer is re-extruded at a temperature of from 150°C to 280°C and at a screw speed of from 10 to 50 rpm.

AMENDED SHEET

12. The process of Claim 11 wherein the polymer is re-extruded at a temperature of from 180°C to 270°C and at a screw speed of from 20 to 40 rpm.

13. An elastomeric polymer obtained by the process of any of the preceding claims.

14. The process of Claim 1 wherein the prepolymer comprises a polyurethane prepolymer (A) having a functionality of 2 and a molecular weight less than or equal to about 10,000 and a second polyurethane prepolymer (B) having functionality of greater than 2, and a molecular weight of less than or equal to about 12,000;

15. The process of Claim 1 wherein: prepolymer A has a monomer content of less than 20% and a molecular weight of from 2,000 to 10,000; prepolymer B has a monomer content of less than 20 % and a molecular weight of from 3,000 to 12,000; the chain extender is a diol having primary hydroxyl functionality and a molecular weight of from 50 to 8,000.

16. The process of Claim 15 wherein: prepolymer A is included at 90% by weight and, prepolymer B is included at 10% by weight.

17. The process of any of Claims 14 - 16 wherein: the chain extender is included such that the ratio of isocyanate to hydroxyl functionality is from about 1.00 to about 100.

18. The process of Claim 17 wherein the chain extender is included such that the ratio of isocyanate to hydroxyl functionality is from 1.00 to 10.0.

19. The process of Claim 18 wherein the chain extender is included such that the ratio of isocyanate to hydroxyl functionality is from 1.50 to 2.00.

20. The process of any of Claims 14 - 19 wherein prepolymer B has a functionality of 2 to a 6.

21. The process of Claim 20 wherein prepolymer B has a functionality of 2 to 3.