Polyurethane prepolymers and elastomers.

Proprietor: W.L. GORE & ASSOCIATES, INC.
555 Paper Mill Road
P.O. Box 9329
Newark Delaware 19711(US)

Inventor: Henn, Robert Lyon
2126 Coventry Drive
Wilmington Delaware 19810(US)

Representative: Kador & Partner et al
Corneliusstrasse 15
D-80469 München (DE)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).
Description

This invention relates to a reactive polymer system, as defined in claim 1. Moreover it relates to the use of the polymer system as defined in claims 7 to 10 as well as to a product obtained by curing the polymer system.

It has hitherto been known to prepare polyurethane polymers having elastomeric properties by three different chemical routes, characterized principally on the basis of processing considerations. These three groupings of elastomers are distinguished by processing as a liquid, millable-rubber or thermoplastic.

The building blocks generally employed in polyurethane technology, the isocyanate species, the polyol and chain extender are well known in the art. Depending on the equivalency ratios employed using these building blocks, various characteristics are achieved that dictate both the processing techniques to be employed to achieve the final desired product, and the properties of the final product. Figure 1 illustrates, in a triangular co-ordinate plot, the percentage equivalents of isocyanate, polyol and chain extender utilized in a general way in prior polyurethane elastomer technology.

Region A of Figure 1 delineates the equivalency ratios commonly employed to obtain a chain-extended, segmented, high-molecular-weight thermoplastics polyurethane exhibiting elastomeric properties. The theoretical maximum molecular weight in this reaction (one-shot or prepolymer) of difunctional reagents is achieved when the equivalency ratio of the diisocyanate to active hydrogen species (polyol and chain extender) is one. Thus, thermoplastic polyurethanes are substantially centered around the region of 50 percent equivalents of isocyanate.

The thermoplastic route to a solid polyurethane elastomer can be subdivided into two classifications: those materials completely soluble in certain solvents and containing no chemical crosslinks before and after processing, and those materials possessing no initial crosslinks, but which form a lightly crosslinked structure after a heated post-cure.

The former class is the more predominantly encountered and is most commonly made by the reaction of essentially equivalents of isocyanate and active hydrogen functionality or a slight excess of the active hydrogen component. Products from this class have the drawback that they are inherently sensitive to particular solvents and will swell extensively in some solvents and dissolve in others. This limits their applications in some areas of application such as coatings, adhesives and sealants.

In the second class of thermoplastic polyurethanes, the synthesis is similar but a slight excess of isocyanate is employed to generate a final polymer having a small amount of unreacted isocyanate groups. These isocyanate groups are then available for crosslinking the final polymer through aliphathane and biuret formation. The crosslink density is low by this method and the final thermoplastic polyurethane polymer must be given a heated post-cure to "activate" these residual "dormant" isocyanate groups.

The processing of either class of thermoplastic polyurethanes may proceed by melt-processing techniques and, in the former class, by solution techniques. Melt processing, such as injection molding, extrusion and calendaring, generally requires fairly sophisticated equipment and high temperatures frequently approaching degradation temperatures of the thermoplastic polyurethane itself. As a rule, these products have a high molecular weight and high melting point. Although low-melting thermoplastic polyurethanes are known, the strength properties of such polymers, including their tensile strength, percent elongation and tear propagation resistance, are generally poor. Solution systems usually require very polar solvents such as tetrahydrofuran, dimethylformamide, dimethylsulfoxide, N-Methyl-2-Pyrrolidone (M-Pyrol), which arouse such concerns as environmental factors and the higher cost for solvents and energy.

The millable rubber route to a solid polyurethane elastomer falls into Region B of Figure 1. To allow conventional rubber processing techniques to be applied to the polymers of this class, the polymers therein are distinguished by their being chain-terminated during synthesis by employing an excess of either the chain extender or the polyol, resulting in a storage-stable, soluble polymer of lower molecular weight than the thermoplastic polyurethanes. To achieve adequate final physical properties, the prepolymer is generally either further chain-extended or crosslinked by employing additional isocyanate, or, where appropriate, cured by sulphur or peroxide.

Liquid processing leading to polyurethanes having elastomeric properties may be further subdivided into the prepolymer existing in Region C of Figure 1, or those referred to commonly as "casting" systems.

Cast polyurethane elastomers are made by a process wherein the reactants are mixed in the liquid state (prepolymer or one-shot route), the reacting mixture is then fabricated into its final form by an appropriate technique such as casting or molding, and the reaction leading to chain extension/crosslinking continues. Complete cure is typically achieved by a hot air post-cure for three to twenty-four hours at 100 °C. In general, after the chain extender has been added and mixed with the prepolymer (or all three components mixed in a one-shot technique), the reaction of these species limits the subsequent pot life to
several minutes. Because this method involves the mixing of two or more liquids, which are all generally of low molecular weight, it is found that initial physical properties of the system are poor until the curing proceeds to some degree. The equivalency ratios of isocyanate:polyol:chain extender employed in cast polyurethane elastomers places most of those systems close to the region characteristic of thermoplastic polyurethanes, generally with a tendency to a slight excess in isocyanate, although, in principle, these systems may employ quite varied equivalency ratios.

Alternatively to the chain extension of the prepolymer, as discussed previously, the prepolymer, Region C of Figure 1, has been utilized directly. Curing is normally achieved by chain extension of the prepolymer through the reaction of isocyanate groups with water and crosslinking by allophanate and biuret formation. It is in this use that a distinguishing feature is observed between the polyester prepolymer and the polyether prepolymer.

The physical form of these prepolymer ranges generally from a viscous liquid to a waxy, low-melting solid, dependent usually upon whether a polyester or polyester polyl has been employed, respectively. In general, polyether prepolymer systems do not exhibit any of their final physical properties until substantially along in the cure cycle. Many polyester prepolymer systems, due to the inherent tendency of the polyester segment to crystallize, exhibit many of their final physical properties early in the cure cycle. This processing characteristic of polyester prepolymer limits many of their industrial applications, wherein some integrity, “green strength”, low flow or similar characteristics are required.

Another class of polyurethanes yielding cured polymers having elastomeric properties are those provided by a “blocked” isocyanate, “one-package” method, in which a polyl is employed as a mixture with a polyisocyanate masked with a blocking agent. The blocked isocyanate method presents disadvantages in that it requires relatively high temperatures for curing to eliminate the blocking agent. When the blocking agent remains partially in the resulting cure polymer, the agent will adversely affect the physical properties of the elastomer and cause environmental pollution in association with the scattering of the agent. These disadvantages permit limited use of the resulting resin.

Although limited, there are some prior polyurethane elastomers that would fall into the equivalency ratios of isocyanate, polyl and chain extender represented by Region D of Figure 1. Those elastomers from Region D are generally characterized by having an excess of the isocyanate species. The preponderance of the elastomers from this region are fabricated according to the casting techniques described above. As mentioned, a limitation to the casting technique has been the limited pot life after all reagents are admixed.

Driven by environmental restrictions, the high cost of solvents and the energy to drive them off, as well as the increased awareness of the toxicity of many solvents, the past decade has seen a trend to higher solids systems for adhesives, coatings and so forth. The difficulty in 100 percent solids systems has been in achieving certain physical characteristics such as green strength with processing characteristics that do not need highly specialized equipment.

Numerous attempts have been made to prepare useful polyurethane elastomers, which are both melt-processable and have acceptable final physical properties, from a polyl of polyoxypropylene. Systems having the chemical resistance to hydrolysis or polyether urethanes, and which possess both the economics of low temperature melt processing and lower rate material cost of the polyoxypropylene glycol over the commonly employed poly(oxytetramethylene) glycol and acceptable physical characteristics, would be strongly desired.

Likewise, numerous attempts have been made to prepare useful polyurethanes, which are melt processable and have acceptable physical properties, from a polyl of polyoxyethylene. In U.S. Patent 3,901,852 successful systems were prepared within the narrow window of both a substantially balanced weight ratio of hard segment to soft segment and an isocyanate to active hydrogen equivalency ratio of approximately 1:1. This is limiting however, particularly when it is desired to produce products wherein the polyoxyethylene content influences other characteristics of desired products, such as hydrophilicity.

In U.S. Patent 3,165,566 a polyurethane is described comprising polyester, isocyanate and glycol units. It does not show a two-phase morphology.

Historically it has been difficult to obtain required physical characteristics such as ultimate tensile strength, ultimate elongation, modulus of elasticity, tear strength, and abrasion resistance in a highly hydrophilic polymeric coating which is useful and commercially attractive. This becomes even more difficult if the economics require melt processability. Specifically, films of highly hydrophilic polymers have tended to be weak and either easily torn or damaged by abrasion and/or flex, especially when swollen with water. Accordingly, there is a current need to produce melt processable systems having increased hydrophilicity without the heretofore concomitant deterioration in physical properties.
It is well known in the art that polyurethane polymers exhibit excellent elastomeric properties, particularly those of the (AB)n segmented block copolymer type, where the polyol soft segment (A) alternates with the polyurethane hard segment (B). It is widely accepted that the unique properties of these copolymers are directly related to the two-phase microstructure which exists when the hard and soft segments phase-separate, the hard segments forming domains which act as a reinforcing filler and pseudo-crosslink the polymeric network.

Accordingly, it is an object of the present invention to overcome the difficulties alluded to hereinabove and provide storage-stable, moderate-temperature melt-processible, one-component, 100 percent solids, reactive polyether polyurethane prepolymer which, when cured, yield elastomers possessing the excellent physical properties typical of the (AB)n type segmented urethane copolymers.

A reactive polymer system being an opaque solid at room temperature and having a two-phase morphology comprising a reactive, segmented polyether polyurethane prepolymer is provided, said prepolymer comprising the reaction product of:

(i) a poly(alkylene ether) polyol having a number average molecular weight of from 600 to 3500 and having a functionality of at least 2;
(ii) an organic isocyanate having a functionality of at least 2; and
(iii) a low-molecular weight chain extender having a molecular weight in a range lower than 500 and having a functionality of at least 2, wherein the reactants are employed in such proportions so as to satisfy the following equations:

\[
\frac{Eq_{NCO}}{Eq_{OH} + Eq_{CE}} \geq 1.1
\]

(b) \( Eq_{OH} \geq Eq_{CE} \)
(c) \( Eq_{CE} > 0 \),

wherein \( Eq_{NCO} \) denotes the equivalents of the isocyanate employed and \( Eq_{OH} \) and \( Eq_{CE} \) denote the respective molar equivalents of the polyol and chain extender employed; and wherein the reaction product of the isocyanate and chain extender provides hard segments and the polyol provides soft segments, said hard segments being incompatible with said soft segments;

the reactive polymer system having a two phase morphology with a hard segment phase comprising domains of the hard segments of the prepolymer and a soft segment phase comprising domains of the soft segments of the prepolymer and whereby the hard segment phase is dispersed within the soft segment phase.

Preferred embodiments of the invention are defined in subclaims 2 to 6.

The prepolymer is useful as a sealant, an adhesive and as a coating on various substrates, as well as in the form of various shaped articles such as films, tubes and rods. Compositions including this prepolymer are useful in electrical cable insulation.

The prepolymer is melt-processible at low temperatures.

When cured, the prepolymer polymerizes to an elastomer having excellent physical properties such as tensile strength, elongation, abrasion resistance and tear strength.

Where the polyol is poly(oxyethylene) glycol, superior moisture vapour transmission rates are achieved, and when elastomeric films are formed as composites with various textiles or other substrates such composites are especially useful in rain protective garments.

Figure 1 is a triangular coordinate plot illustrating the percentage equivalents of isocyanate, polyol and chain extender generally utilized in polyurethane elastomer technology.

Figure 2 is a schematic diagram of a process and apparatus used in coating a textile fabric with an elastomer of this invention.

Figure 3 contains schematic formulae (I) to (XI) referred to in the following description.

For convenience and clarity in teaching the present invention, the following description is limited to difunctional compounds and to a macroglycol being of a poly(alkylene ether) glycol. This should be recognized as not to be limiting the scope or spirit of the invention. As will be apparent to those in the art, functionalities greater than two may be used to tailor desired properties, such as compression-set,
depending upon the application. Likewise, the polymeric backbone can be other than poly(alkylene ether) as desired or required by the application.

It is well accepted in the art that the excellent physical properties of polyurethane elastomeric polymers are due to the two-phase microstructure which exists when the hard and soft segments in the system phase-separate. This invention provides for a novel, one-component system for introducing effective hard and soft segments into a polyurethane polymer.

This invention provides prepolymers having suitable hard and soft segments. These polyurethane prepolymers have an excess of the reactive isocyanate functional group depicted graphically as falling within Region D of Figure 1 and expressed mathematically by the equation (a) set forth above.

The prepolymers herein are the reaction products as stated above. However, for the purpose of further clarification, it is believed that they may be represented by the following formula (I):

\[
OCN-Y-NH-C-0-X-0-(C-NH-Y-NH-C-Z)-C-NH-Y-NH-C-0-n-0-X-0-C-NH-Y-NCO (II)
\]

wherein:

- X is a residue derived by the elimination of the two hydroxyl groups from a poly(alkylene ether) glycol having a molecular weight in a range of 600 to 3500;
- Y is a residue derived by the elimination of two isocyanate groups from an organic diisocyanate; and
- Z is a residue derived by the elimination of two active hydrogens from a low-molecular-weight bifunctional chain extender having a molecular weight in a range lower than 500;

and m and n are each positive real numbers.

The formula (I) may be more generally represented by the schematic formula (II) in Figure 3 of the drawings wherein:

\[\square\]

is the residue of having reacted an organic diisocyanate with the adjacent organic species, as familiar to those skilled in the art, and if no adjacent species is present, as in pendant

\[\square\]

at the end of a chain above, then the unreacted isocyanate functional group is assumed present,

\[\sim\]

is the residue derived by the elimination of the two hydroxyl groups from a poly(alkylene ether) glycol having a molecular weight in a range of 600 to 3500;

\[\diamond\]

is the residue derived by the elimination of two active hydrogens from a low-molecular-weight bifunctional chain extender having a molecular weight in a range lower than 500;

and m and n are again each positive real numbers.

By way of example, if a poly(oxyethylene) glycol of molecular weight 1450 is reacted with 4,4’-diphenylmethane diisocyanate and 1,4-butane diol according to the teaching described later at an equivalency ratio of 4:2:1, isocyanate: macroglycol: chain extender, then from above m = 1 and n = 1 and in formula (I):
\[ X = \text{-} \text{CH}_2\text{CH}_2\text{-}(\text{O-CH}_2\text{CH}_2\text{)}_p \]

such that \( p \) yields a molecular weight of about 1450.

\[ Y = \text{-} \text{CH}_2\text{-CH}_2\text{-} \]

and

\[ Z = \text{-} \text{O-CH}_2\text{CH}_2\text{CH}_2\text{-O-} \]

or schematically as (III) in Figure 3 of the drawings.

Or, further, if the same species were reacted according to the teachings herein at an equivalency ratio of 5:2:2, isocyanate: macro glycol: chain extender, then \( m = 2 \) and \( n = 1 \) and schematically as (IV) in Figure 3 of the drawings.

Or, further, if the same species were reacted according to the teachings herein at an equivalency ratio of 6:3:2 then \( m = 1 \) and \( n = 2 \), the product would be schematically (V) in Figure 3 of the drawings.

It is generally recognized by those practiced in the art that the soft segment is that provided by the macro glycol, herein the poly(alkylene ether) glycol, and the hard segment is provided by the reaction product of the organic isocyanate and the low-molecular-weight bifunctional chain extender. According to formula (I) this is represented by:

According to the schematic representation set forth herein the symbol:

\[ \sim \]

would represent the soft segment as described, and a collection of symbols such as

would represent the hard segment as described, so that a prepolymer made as the reaction product of an equivalency ratio of 5:2:2 organic isocyanate; poly(alkylene ether) glycol; chain extender would be understood schematically as (VI) in Figure 3 of the drawings.

It should be recognized, as will be apparent to those skilled in the art, that the isocyanate functional group is highly reactive and dependent on such things as reaction conditions, the species employed, unexpected contaminants and so forth, which will all affect the resulting reaction product.

The prepolymers of this invention can be prepared by procedures conventional in the art for the synthesis of polyurethane elastomers. Such procedures include the prepolymer procedure in which the isocyanate is reacted with the polyl in a first step and the isocyanate-terminated prepolymer so produced is subsequently reacted with a stoichiometric deficiency of chain extender to result in a prepolymer having equivalency falling within Region D of Figure 1 and mathematically satisfying equations (a), (b) and (c), above. The one-shot procedure in which all the reactants are brought together simultaneously is also
suitable in the synthesis of the prepolymer of this invention. The prepolymer route is the preferred procedure for preparing the reactive, phase-separating polyether polyurethane prepolymer of this invention. In a most preferred embodiment, to be described in detail below, the prepolymer of this invention is prepared by a slow addition of polyl to liquid disiocyanate in such a manner as to favor a narrow molecular weight distribution of isocyanate-terminated prepolymer, followed by the addition of the stoichiometric deficiency of chain extender.

Whichever method of preparation is employed, it is found, surprisingly, that the reactive prepolymer of this invention have excellent storage stability without the need for stabilization typically employed with other polyurethane prepolymer, such as that provided by acyl halides. Despite being stored at room temperature as a 100 percent solids system and having a concentration of urethane and/or urea groups in the presence of the reactive isocyanate species, shelf stability is exhibited by the percent free isocyanate remaining consistently close to the theoretical percent isocyanate calculated and by the ability to continue to be able to process these systems over an extended period of time without seeing gel formation. Further, and equally surprisingly, it has been found that closely related polyurethane prepolymer, prepared in identical fashion and from the same reactants as set forth above, but using proportions of reactants which do not meet the requirements of equation (b), supra, shorn markedly inferior shelf stability and a difficulty in achieving the theoretical percent isocyanate during the synthesis thereof.

It is believed that this remarkable difference in shelf stability between the prepolymer of this invention on the one hand, and, on the other hand, the related prepolymer which differ only in that the proportions of reactants used therein do not meet the requirements of equation (b) above, is attributable to the location of the hard segment(s) in the prepolymer chain. By the synthesis procedures employed herein the prepolymer satisfying all the equations (a), (b) and (c), supra and thus falling within Region D1 of Figure 1, are believed to exhibit the hard segment(s) internal to the prepolymer chain sandwiched between the soft segments. Conversely, by the synthesis procedures employed herein, the prepolymer satisfying equations (a) and (c) but not (b), supra, and thus falling within Region D2 of Figure 1, are believed to exhibit hard segments pendant on the prepolymer chain sandwiching soft segment(s) between them.

By way of illustration, a shelf-stable prepolymer of this invention would be provided by the reaction product of an organic disiocyanate (B) with a poly(alkylene ether) glycol (A) and low-molecular-weight bifunctional chain extender (C) at an equivalency ratio of 4:2:1 respectively, which satisfies the above cited equations. This prepolymer would be schematically illustrated as (VII) in Figure 3 of the drawings.

A prepolymer made in the same manner and with the same reagents as above, but not satisfying equation (b), would be provided at an equivalency ratio of 4:1:2. This prepolymer would be expected to provide for poor shelf stability and would be schematically illustrated as (VIII) in Figure 3 of the drawings.

It is believed that the requirement that the prepolymer of this invention mathematically satisfy equation (b) set forth above is equivalent to the structural requirement of internal hard segments.

Additionally, it has been found that not all internal hard segments provide for shelf stability of prepolymer even when equations (a), (b) and (c) have been satisfied. It appears that not only must the hard segment be located internal to the prepolymer chain but the hard segment must be a “suitable” hard segment. A suitable hard segment is one that induces phase-separation of the hard and soft segments found in the prepolymer chain. It is believed that such phase-separation results in domains of hard segments dispersed in the soft segments. This two-phase morphology may be schematically illustrated with a 4:2:1 prepolymer system as (IX) in Figure 3 of the drawings.

This two-phase morphology is believed to be the source for the prepolymer stability of this invention. It appears to effectively reduce the prepolymer chain mobility and diminishes the effective concentration of the active hydrogen species available for reaction with isocyanate through the hard segment domain reducing those active hydrogen species available to the interface between the two domains.

A suitable hard segment is one that effects phase-separation of the hard and soft segments of the prepolymer of this invention. Factors influencing phase-separation in (AB)n type thermoplastic polyurethanes have been extensively studied and these teachings can be employed for the purpose of achieving suitable hard segments for the prepolymer of this invention. See for example the review in, Multiphase Polymers, Gould, Robert ed., Chapter 1, "Morphology and Properties of Segmented Copolymers", 1979, pps 3-30. In general, the factors yielding a two-phase structure are those resulting in thermodynamic incompatibility between the hard and soft segments, which depends on the segment type, segment length, segment compatibility, chemical composition, method of fabrication and the ability of the segments to crystallize.

Because there are numerous factors influencing the tendency of hard segments to phase-separate into domains dispersed within the soft segments, it will be apparent to one skilled in the art that there will not be a precise dividing line between “suitable” hard segments and those not "suitable" within the scope of this invention. Each condition and situation must ultimately be evaluated independently.
As set forth above, the hard segment of the segmented prepolymer is the residue derived by the reaction of the organic diisocyanate and the low-molecular-weight bifunctional chain extender. For a suitable hard segment, this reaction product must produce a hard segment that is thermodynamically incompatible with the soft segment or polyol utilized. In general, the organic diisocyanates and low-molecular-weight bifunctional chain extenders known in the art may be employed in the invention herein so long as the condition of thermodynamic incompatibility is satisfied.

It has been found that the preferred organic diisocyanates (B) to be used for the prepolymer in accordance with this invention are those exhibiting several or all of the following characteristics: bulky, symmetrical around the isocyanate functional groups, rigid, aromatic, crystalline and of high purity. By way of example, are:

- 4,4’-diphenylmethane diisocyanate,
- cyclohexanedimethylenecyanurate, and
- p-phenylene diisocyanate,
- 1,5-naphthalene diisocyanate,
- toluene diisocyanate, and
- p-xylene diisocyanate, and
- hexamethylene diisocyanate,
- 4,4’-dicyclohexylmethane diisocyanate,
- 4-bis(isocyanatomethyl) cyclohexane,
- p-tetramethylene diisocyanate, and
- m-tetramethylenediisocyanate.

The organic diisocyanates may be employed singly or in admixture with other.

The preferred low-molecular-weight bifunctional chain extender to be used for the prepolymer in accordance with this invention has a molecular weight in the range from 40 to 500 and exhibits several or all of the following characteristics: symmetrical, rigid, free from branching, of low molecular weight, aromatic, crystalline, and of high purity. It has been found, surprisingly, that a broader range of chain extenders than expected may be utilized in accordance with this invention and still yield a prepolymer with the characteristics as set forth herein. Suitable chain extenders may come from the following classes of compounds:

(i) aromatic, open-chain aliphatic and cycloaliphatic glycols and combinations thereof,
(ii) aromatic diamines,
(iii) alkanolamines and hydroxy arylamines, and
(iv) open-chain aliphatic and cycloaliphatic diamines which are thought to be satisfactory given an appropriate synthesis procedure.

By way of example are:

- 1,4-butanediol,
- 1,6-hexanediol,
- hydroquinone di(2-hydroxyethyl)ether,
- bis-(2-hydroxyethyl) bisphenol A, bis(2-hydroxypropyl) bisphenol A,
- bis(2-hydroxypropyl) isophthalate,
- bis(2-hydroxyethyl) carbamate,
- 1,2-bis(2-aminophenyl)thio)ethane,
- trimethylene glycol di-p-aminobenzoate,
- resorcinol di(2-hydroxyethyl)ether,
- 1,4-cyclohexanediol,
- 4,4’-dihydroxy diphenyl sulfone,
- 4,4’-methylenediphenyl bis(o-chloroaniline),
- phenylene diamine,
- methylene bis(aniline),
- ethanolamine,
- N,N’-bis-(2-hydroxyethyl) dimethylhydantoin,
- ethylene diamine,
- butane diamine,
- and the like. The low-molecular-weight bifunctional chain extenders (C) may be used singly or in admixture with each other.

The prepolymer in accordance with the present invention has a molecular weight in the range from 600 to 3500. The term "poly(alkylene ether) glycol" as used herein represents a macroglycol of a poly(alkylene ether) backbone with two terminal hydroxy groups. More generally, the term denotes a difunctional polyether terminated with hydroxy groups. These compounds are ordinarily derived from the polymerization of cyclic ethers such as alkylene oxides or dioxolane or from the condensation of glycols. They are sometimes known as poly(alkylene) glycols, poly(alkylene oxide) glycols, polyglycols, polyoxyalkylenes, n-polyoxyalkylene diols.

They may be represented by the formula (X):

\[
\text{HO-(RO)}_r\text{-H} \quad (X)
\]

wherein R denotes an alkylene radical and r is an integer greater than 1.

In the polyethers useful in this invention, r is sufficiently large that the poly(alkylene ether) glycol has a molecular weight of 600 to 3500. Not all the alkylene radicals represented by R need be the same. Macroglycols formed by the copolymerization, random or block, of a mixture of different alkylene oxides or glycols may be used, or the polyglycol may be derived from a cyclic ether such as dioxolane, which results in a product having the formula:

\[
\text{HO(CH}_2\text{OCH}_2\text{CH}_2\text{O)}_r\text{-H}
\]

The alkylene radicals may be straight-chain or may have a branched chain as in poly(propylene ether) glycol. Typical representatives or this class of compound are polytetramethylene glycol, poly(propylene ether) glycol, poly(oxymethylene) glycol and the copolymers resulting from the block or random copolymerization of ethylene oxide and propylene oxide and those resulting from the copolymerization of tetrahydrofuran and ethylene oxide. The poly(alkylene ether) glycols may be used singly or in admixture with each other.
It is further contemplated that prepolymers made in accordance with this invention may be prepared from other polyalkylene ether glycols familiar to those skilled in the art providing advantages herein delineated.

Although the most preferred prepolymers of this invention are prepared from difunctional compounds, to achieve certain physical properties, as will be apparent to those skilled in the art, the prepolymers may be further tailored by incorporating species of higher functionalities in various amounts. The higher functionality, and thus higher branching in the prepolymer, may be introduced to the system through the polyl, isocyanate or chain extender.

The prepolymers of this invention, even at low molecular weights, are solid at room temperature, whereas prior prepolymers bearing no hard segment or non-soluble hard segments are not generally found to be solid unless at much higher molecular weights. This solid nature may be attributed to the higher ordering and increased molecular interaction of the prepolymer system that occurs when the hard segments aggregate in domains. It has been determined, generally, that those systems which yield suitable hard segments as defined herein phase-separate at room temperature to a sufficient degree that the overall appearance of the prepolymer is a highly opaque, white solid. It is believed that this opacity, in those systems devoid of any crystallinity in the soft segment, is due to the differences in the refractive indices of the hard and soft segment domains. It has been found that this opacity, introduced by the two-phase morphology of the prepolymers of this invention, may be used to qualitatively determine the degree of phase-separation that is occurring and, thus, in turn, may be used as a tool of first approximation to evaluate the suitability of the hard segments formed.

It is found, surprisingly, that the phase-separating polyurethane prepolymers of this invention provide unique melt flow properties compared to their thermoplastic polyurethane counterparts having hard segments. It has been found that these phase-separating prepolymers are low-melting and, as such, may be melt-processed at lower temperatures than can typical thermoplastic polyurethanes. In addition, these prepolymers generally show a sharp decrease in melt viscosity soon after the melting of the hard segment domains. Once sufficient energy is provided to the phase-separating prepolymer system to remove the intermolecular interaction provided by the hard segment domain and allow for phase-mixing, the low molecular weight of the prepolymer affords significantly lower chain interaction and, therefore, lower viscosity.

A significant feature provided by the low-melting characteristic of the prepolymers herein is the ability to utilize hard segments containing urea functionality. It is known that hard segments resulting from diamine chain extenders generally provide improved physical characteristics over their glycol counterparts. However, the increased hydrogen bonding encountered in such urea-containing hard segments frequently requires heating a solvent-free system to the point of degradation thus necessitating use limited to solution systems.

Low-melting thermoplastic polyurethanes, per se, are known. However, known low-melting thermoplastic polyurethanes do not possess generally good physical property profiles. Known low-melting thermoplastic polyurethanes have been prepared, for example, by employing a reaction mixture containing the difunctional reactants and large amounts of monofunctional compounds having an active hydrogen such as alcohols or amines. Such a reaction mixture results in the production of relatively short-chained polyurethanes which, understandably, exhibit a poor property profile. Additionally, low-melting thermoplastic polyurethanes have been prepared by the incorporation of glycols which produce hard segments having a low melt temperature, but a concomitant poor physical property profile.

In polyurethane elastomers, it is commonly recognized that for good physical characteristics in use, it is preferred to have a soft segment having a glass transition temperature ($T_g$) well below the expected use temperature and a hard segment having a melt temperature ($T_m$) well above the expected use temperature. The latter temperature has been understood to control the melt temperature of the overall thermoplastic polyurethane. A surprising feature of the prepolymers of this invention is the magnitude to which this melt temperature of the hard segment is suppressed, allowing for low melt characteristics. Further, it has been determined that the prepolymers of this invention have melt flow characteristics in many cases well below that indicated by what would be considered the hard segment melt temperature ($T_m$). More specifically, Thermal Mechanical Analysis and Melt Flow Index indicate a softening point and melt flow below the endotherm associated with $T_m$ determined by Differential Scanning Calorimetry. Equally surprising is the finding that, after allowing the prepolymer to cure, even with water, the hard segment melt temperature ($T_m$) has increased to appreciably higher temperatures, yielding cured polyurethane elastomers having exceptional physical properties and in some cases being capable of melt processing, although at significantly higher temperatures as typical of other thermoplastic polyurethanes in the art. It is possible that this characteristic of the phase-separating, segmented prepolymers of this invention is due to both the low molecular weight and phase mixing and/or lower ordering in the prepolymer with enhanced phase-
separating and/or higher ordering along with higher molecular weight once the prepolymer is cured.

A cured polymer obtained by curing a prepolymer of this invention may be a thermoplastic polyurethane, having a melt-processing temperature substantially in excess of the melt-processing temperature of the prepolymer.

As mentioned, supra, thermal analysis, namely differential scanning calorimetry (DSC), thermal mechanical analysis (TMA), melt flow index (MFI), thermal gravimetric analysis (TGA) and gradient hot plate (GHP), was utilized to detect and investigate the contribution of the separate phase domains and thermal characteristics discussed. There has been much published in the literature for analyzing segmented polyurethanes via these thermal techniques. See, by way of example, the review and its references in "Multiphase Polymers, Gould, Robert ed., Chapter 4, "Thermoplastic Polyurethane Elastomer Structure - Thermal Response Relations", 1979, pps 83-96.

The segmented polyurethane elastomers produced from the prepolymers of this invention exhibit excellent physical properties typical of (AB), segmented polyurethane copolymers, as measured by ultimate tensile strength, elongation, modulus of elasticity and tear strength. The prepolymers of this invention may be cured by procedures conventional in the art for the curing of isocyanate-terminated prepolymers. By way of example are moisture, blocked amines, oxazolidines, epoxies, triisocyanurate ring formation, allophanate and biuret crosslinking. Dependent upon the curing technology employed, the resulting polyurethane elastomer once curing is accomplished may be either a thermoset polyurethane or a thermoplastic polyurethane of higher melt temperature.

As will be apparent to one skilled in the art, the final physical properties of the elastomers of this invention may be altered considerably by altering the identity, stoichiometry and molecular weight of the species reacted. As such, the determination of a precise boundary between cured prepolymers made so as to satisfy equations (a), (b) and (c), supra, exhibiting elastomeric or plastic properties, is practically impossible. The amount of the reactants employed in the prepolymer depends, inter alia, on the desired properties of both the prepolymer and the final cured polyurethane.

A unique benefit is provided by the prepolymers of this invention. That is, they may be used directly as a one-component, 100 percent solids system, and allowed to cure yielding exceptional final physical properties. In addition, the prepolymers herein may be used in combination with other resins and/or curing techniques to provide further unique results.

By way of example, techniques such as polymer alloying through polyblends or interpenetrating polymeric networks may be employed. Since the prepolymers of this invention are so versatile, they may be tailored to yield different melt-processing temperatures by considering such factors as cited above; thus a prepolymer may be "tailored" to suit the processing requirements of the other resin, and as such be more easily incorporated. By way of example, the prepolymers herein have been successfully incorporated into a heavily filled ethylene acrylic resin at less than 5 percent by weight with a surprising doubling of the tear strength previously possible. It is further contemplated that the prepolymers of this invention would prove useful as polymer blends, alloys, and interpenetrating polymeric networks with e.g. polyacrylates, polymethacrylates, polyamides, polyamines, polysulfides, polyethers, polyesters, polycarbonates, polychloroprene, poly(vinyl chloride), polysiloxanes and vinyl polymers.

A unique and worthwhile result provided by the phase-separating segmented, polyether polyurethane prepolymers of this invention is the good intermediate physical property profile of the polyether prepolymers prior to curing. The polyether prepolymers conventionally available in the prior art do not generally obtain good physical property characteristics until substantially into their cures. As a result of the segmented, phase-separating nature of the polyether prepolymers of this invention, a rapid increase in apparent crosslinking occurs when the prepolymer is allowed to cool during processing. This results in high intermolecular interaction yielding a high effective viscosity or what is commonly referred to as "green strength". Thus, these prepolymers develop some of their good physical properties prior to curing through the isocyanate functional group.

A prepolymer of this invention may be formed into a shaped article such as a tube or rod, and when cured the shaped article may have a tensile strength in at least one direction exceeding (500 psi) 3.45 MN/m² and preferably exceeding (5000 psi) 34.47 MN/m².

A curved film produced from a prepolymer of this invention may have one or more of the following physical characteristics:

(a) a tensile strength in at least one direction exceeding (500 psi) 3.45 MN/m² preferably exceeding (1000 psi) 6.89 MN/m², more preferably exceeding (2000 psi) 13.79 MN/m² and most preferably exceeding (5000 psi) 34.47 MN/m²;
(b) an elongation greater than 200 percent;
(c) high abrasion resistance;
(d) a tear initiation strength exceeding (170 pli) 29.7 kN/m;
(e) a tear propagation strength exceeding (0.10 lb) 0.44N at 300 micrometres thickness and/or exceeding (0.02 lb) 0.089 N at 200 micrometres.

Further, and surprisingly, the prepolymer of this invention exhibit the desirable tendency to be low-foaming when cured with water, particularly as compared to the prepolymer more conventional in the art. This is particularly true in cases in which there is a higher tendency for the segments employed to phase-separate. This yields improved physical properties at larger cross-sectional thicknesses than would be possible without the reduced foaming.

An additional unexpected result was found in the prepolymer of this invention prepared from polyoxyethylene glycol. In the segmented, phase-separating polyoxyethylene prepolymer containing suitable hard segments, it was found that once cured, films thereof showed, simultaneously, an increase in moisture vapor transmission rate and physical property profile. Historically, it has been difficult to obtain the required physical characteristics, i.e. ultimate tensile strength, ultimate elongation, modulus of elasticity, tear strength and abrasion resistance, in a highly hydrophilic polymer to allow it to be useful commercially. Specifically, films of highly hydrophilic polymers have tended to be weak and either easily torn or damaged by abrasion and/or flex, especially when swollen with water.

Historically, there was a need to find the most suitable compromise between moisture vapor transmission and physical properties. The prepolymer route defined herein provides an elastomer having a high moisture vapor transmission rate without a concomitant deterioration in physical properties, but, rather, an increase thereof. This increase in moisture vapor transmission rate and physical properties is believed to be the result of the heterogeneous structure in the polyurethanes made from these prepolymer. As a result, the polyl glycol segment is "reinforced" by the hard segment domains and a water molecule is provided a shorter effective diffusive path length in the hydrophilic soft domain than what would be experienced in a homophase containing a similar weight percent of the hydrophilic polyl glycol.

Furthermore, the prepolymer route provided herein allows for desirable physical properties and melt processing outside of the limitation of equal balance on a weight basis, between the total soft segments present in the molecule with the total hard segments present therein, disclosed in U.S. Patent 3,901,852. In addition, this invention allows for the polyl glycol content to be greater than the maximum 45 percent by weight of the reaction mixture as disclosed in U.S. Patent 4,367,327, and still have excellent physical properties.

A cured film produced from a prepolymer of this invention wherein the polyol is polyl glycol may have a moisture vapor transmission rate (as hereinafter defined) exceeding 5000, preferably exceeding 10000 and most preferably exceeding 15000 g/m²·24 hours (2 mils) 50.8 micrometers.

The physical properties, characteristics and scope of the reactive, segmented, phase-separating, polyether polyurethane prepolymer of this invention render them well suited for use, among other things, as adhesives, coatings and sealants.

As set forth above, the prepolymer of this invention are preferably made by a prepolymer procedure and most preferably by the batch prepolymer procedure as herein described. The mixing of the reactants can be accomplished by any of the procedures and apparatus conventional in the art. Preferably the individual components are received as urethane grade and, as such, have low moisture content or are rendered substantially free from the presence of water using conventional procedures, for example, by azeotropic distillation, or by heating under reduced pressure at a temperature in excess of the boiling point of water at the pressure employed. The later procedure is preferred to accomplish degassing of the components.

The proportions of the reactants as described herein are consistent with the equivalency ranges defined above.

The diisocyanate is charged to the reaction vessel first at ambient temperature, preferably under conditions that minimize exposure to ambient moisture. The reaction vessel is vacuumed of ambient moisture and blanketed with nitrogen. The diisocyanate in an inert atmosphere of nitrogen is then brought up to a temperature generally from 40 °C to 100 °C, preferably at a minimum temperature just above the melting point of the diisocyanate employed. To the diisocyanate is added the poly(alkylene ether) glycol as a liquid, frequently heated to the same temperature as the diisocyanate. The glycol is added dropwise to the diisocyanate at a rate that allows the glycol to be substantially capped by the diisocyanate at any point in time. That is to say, the actual percent free isocyanate, as measured by a dibutylamine titration or equivalent procedure, approximates to the theoretical percent of free isocyanate expected by the known amount of glycol addition to that point. Subsequent to the addition of the glycol the isocyanate-terminated prepolymer thus formed is heated preferably to the minimum temperature empirically found wherein the prepolymer product of this invention, once formed, can still be stirred in the vessel being employed.
Dependent upon the hard segment being formed, the desired molecular weight and the reaction vessel/stirrer employed, inter alia, this minimum temperature is from about 60 °C to about 150 °C. The bifunctional chain extender, usually at ambient temperature, is charged to the intermediate prepolymer as soon as it is at temperature, or before, wherein the resulting exotherm can be used to assist the reaction mass to reach the desired final temperature. The addition can be at a point wherein the reactivity of the chain extender is sufficiently slow to not cause an increase in viscosity above that which the system can handle as the temperature is increasing. Preferably, the chain extender is charged all at once unless the exotherm results in a temperature increase above that which is desired.

Shortly before and/or after the chain extender has been added, the reaction mass is degassed via vacuum. Typically, degassing may proceed as soon as opacity of the prepolymer begins to appear or, similarly, as the viscosity is seen to increase significantly. The reaction mass is held at temperature until the free isocyanate content decreases to approximately 0 to 20 percent above the value calculated for the theoretical final percent free isocyanate, and then the prepolymer is discharged into suitable containers and sealed under nitrogen to exclude any ambient moisture.

Alternatively, in the preferred batch prepolymer process, the poly(alkylene ether) glycol may be added to the diisocyanate at a rate in excess of that described above in the most preferred procedure, and at a rate so as not to cause an undesired increase in temperature due to the exotherm.

When the prepolymer of this invention are prepared by the less preferred one-shot method, the reactants are brought together at essentially the same time, in any order. Advantageously, the poly(alkylene ether) glycol and the bifunctional chain extender are preblended and fed to the reaction vessel as a single component, the other component being the diisocyanate. This reaction is carried out advantageously within the range of the final reaction temperature specified above for the prepolymer procedure. In general, the prepolymer may be degassed as described previously, at the point of opacity or increased viscosity. The degassed prepolymer is transferred to a suitable container as soon as a free isocyanate content of about 0 to 20 percent above the theoretical end point is obtained.

It is advantageous to minimize the temperature, and time at high temperature, of the reaction mass to avoid undesirable side reactions which may occur, such as the formation of allophanate, biuret and triisocyanurate groups. Such side reactions will cause branching and crosslinking and result in an undesirable elevation of the melting point of the product as well as destroy the order of the segmented system.

It may be desirable, but not essential, to include a catalyst in the reaction mixture employed to prepare the prepolymer of this invention. Any of the catalysts conventionally employed in the art to catalyze the reaction of an isocyanate with a compound containing an active hydrogen can be employed for this purpose. The amount of catalyst employed is generally within the range of 0.02 to 2.0 percent by weight of the reactants.

If desired, the prepolymer of this invention can have incorporated in them, at any appropriate stage of preparation, additives such as pigments, fillers, lubricants, stabilizers, antioxidants, coloring agents and fire retardants, which are commonly used in conjunction with polyurethane elastomers. The same care must be taken to ensure moisture levels of the additives as appropriate in conventional polyurethane prepolymer technology.

As an alternative to the batch process described above, it is contemplated that equally acceptable prepolymer of this invention may be produced continuously, for example, by employing a reaction extruder. Further, it is contemplated that the preferred method, allowing for the high reactivities of the amine functional group in the preparation of the prepolymer herein, would be the use of an impingement style mixer as typically found in reaction-injection-molding mixer heads.

An elastomer-coated fabric can be made with the prepolymer of this invention as shown in Figure 2. Therein, a continuous belt 2 of fluorinated ethylene propylene fluorocarbon polymer passes over heated roller 4 and the liquid polymer 6 of this invention is applied to the belt 2 by a doctor blade 8 to form film 10 thereon. The belt and film are carried over cold roller 12 in the direction of rotation shown by the arrows, and fabric 14 is applied to film 10 in the nip of rollers 12 and 16 as shown. The film has some green strength at this point and is somewhat tacky. The composite textile carrying the film, 18, is stripped from the belt 2 by the peel bar 20 and then the composite proceeds to a conventional cure step, not shown, represented by the arrow shown, thereby producing a fabric coated with the elastomer of this invention.

A fabric having a cured coating produced from a prepolymer of this invention wherein the polyol is polyoxylethylene may have a moisture vapor transmission rate (as hereinafter defined) exceeding 3000 g/m² .24 hours and which exceeds 50 percent and preferably exceeds 75 percent of that of the fabric alone and most preferably is comparable with that of the fabric alone.
A description of the test employed to measure moisture vapor transmission rate (MVTR) is given below. The procedure has been found to be suitable for testing thin (generally less than (10 mils) 254 micrometers) hydrophilic films and composites thereof.

In the procedure, approximately 70 ml of a saturated salt solution of potassium acetate and distilled water is placed into a (4.5 ounce) 130 ml polypropylene cup, having an inside diameter of 6.5 cm at the mouth. An expanded polytetrafluoroethylene (PTFE) membrane, having a Gurley number of 5.5 seconds, a bubble point of (26.8 psi) 185 kN/m², thickness of 25 micrometers and a weight of 12 g per square meter, available from W.L. Gore & Associates, Incorporated, Elkton, Maryland, product designation PN 10300NA, is heat-sealed to the lip of the cup to create a taut, leakproof, microporous barrier containing the salt solution. A similar expanded PTFE membrane is mounted taut within a (5 inch) 13 cm embroidery hoop and floated upon the surface of a water bath. The water bath assembly is controlled at 23 °C plus or minus 0.1 °C, utilizing a temperature-controlled room and a water-circulating bath.

The sample for testing MVTR is mounted taut in a (3 inch) 8 cm diameter embroidery hoop and equilibrated in a chamber having a relative humidity of about 86 percent for 48 hours. The film is then adjusted to be taut in the hoop and is placed face down onto the surface of the floating PTFE membrane.

The cup assembly is weighed to the nearest 1 mg and is placed in an inverted manner onto the center of the test sample.

Water transport is provided by the driving force between the water and the saturated salt solution providing water flux by diffusion in that direction. The sample is tested for 15 minutes and the cup assembly is then removed, weighed again to within 1 mg.

The MVTR of the sample is calculated from the weight gain of the cup assembly and is expressed in grams of water per square meter of sample surface area per 24 hours.

A second cup assembly is simultaneously weighed to within 1 mg and placed onto the test sample in an inverted manner as before. The test is repeated until a steady state MVTR is observed by two repetitive MVTR values. With thin films, this generally requires only two successive tests.

Several thicknesses of film are tested and the values thereof extrapolated to a normalized film thickness of (2 mils) 51 micrometers for the purposes of direct comparison when appropriate.

The abrasion data presented in the examples was conducted as specified in Federal Standard 191, Method 5304 except that the abrasant was a 70-by-50 mesh stainless steel screen. Failure to abrasion was determined by leakage to water under a hydrostatic head test of (30 inches) 76.2 cm for 3 minutes in accordance with Federal Standard 191, Method 5516. Abrasion results are then reported as number of cycles abraded without failure by leakage.

EXAMPLE 1

A prepolymer of this invention was prepared from 196.2 g (1.570 molar equivalents) of 4,4'-diphenylmethane diisocyanate, 386.2 g (0.7847 molar equivalents) of poly(oxytetramethyleylene) glycol having a molecular weight of 1000 and 17.64 g (0.3920 molar equivalents) of 1,4-butadiol using the following most preferred procedure:

The 4,4'-diphenylmethane diisocyanate was added to a 1000 ml jacketed resin kettle at room temperature and the entire flask evacuated with vacuum and purged with dry nitrogen. The 4,4'-diphenylmethane diisocyanate was then heated to 80 °C, melting the diisocyanate. To the diisocyanate was added, with stirring, from an addition funnel at room temperature the poly(oxytetramethylene) glycol. The poly(oxytetramethylene) glycol had been previously degassed by heating at 95 °C under reduced pressure for 2 hours. The poly(oxytetramethylene) glycol was added over 1.5 hours. After an additional 20 minutes the free isocyanate value was found to be 5.6 percent, as determined by a standard dibutylamine titration procedure.

To the isocyanate-capped poly(oxytetramethylene) glycol thus formed was added the 1,4-butanediol in one charge with rapid stirring and nitrogen purge throughout. After 30 minutes, the free isocyanate value was found to be 2.7 percent, and the prepolymer turned from colorless to an opaque white.

The segmented prepolymer (Prepolymer I) so formed was poured warm from the reactor directly into paint cans, blanketed with nitrogen and sealed. Prepolymer 1 maybe schematically illustrated as (II) in Figure 3 of the drawings.

Prepolymer I so formed and packaged was found to be storage-stable after 4 months as exhibited by a stable isocyanate value of 2.6 percent isocyanate throughout, and the ability to process the prepolymer as desired. Further characteristics of this prepolymer shown in Table 1 additional exemplify this invention.

The properties of a moisture-cured film are also provided therein. The cured film was prepared by heating a container of Prepolymer I at 110 °C for 30 minutes, then, using a draw-down bar of a fixed gap of
0.13 mm, casting a film of Prepolymer I directly onto a release sheet similar to the process shown in Figure 2. The film was then cured by placing it in a 90-100 percent relative humidity chamber at ambient temperature.

### TABLE 1

<table>
<thead>
<tr>
<th>PROPERTIES OF PREPOLYMER I</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening Point (per Perkin-Elmer TMA probe 0209, 2 g load)</td>
<td>62 °C</td>
</tr>
<tr>
<td>Melting Index</td>
<td></td>
</tr>
<tr>
<td>2.16 kg at 65 °C</td>
<td>2.31 g/10 minutes</td>
</tr>
<tr>
<td>2.16 kg at 70 °C</td>
<td>80.6 g/10 minutes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PHYSICAL PROPERTIES OF A CURED FILM OF PREPOLYMER I</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>0.086 mm</td>
</tr>
<tr>
<td>Tensile strength at break (per ASTM D882-81)</td>
<td>(4600 psi) 31.7 MN/m²</td>
</tr>
<tr>
<td>Elongation at break (per ASTM D882-81)</td>
<td>510 percent</td>
</tr>
<tr>
<td>Modulus of Elasticity (per ASTM D882-81)</td>
<td>(4400 psi) 30.3 MN/m²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tear strength</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation (per ASTM D1004-66)</td>
<td>(240 psi) 42.0 kN/m</td>
</tr>
<tr>
<td>Propogation (per ASTM D1938-67)</td>
<td>(0.077 lb) 34.9 g at 0.086 mm</td>
</tr>
<tr>
<td>Softening Point (TMA)</td>
<td>205 °C</td>
</tr>
<tr>
<td>Melting Index:</td>
<td></td>
</tr>
<tr>
<td>7.06 kg at 193 °C</td>
<td>9.95 g/10 min.</td>
</tr>
</tbody>
</table>

**Comparative Example 1**

To illustrate the "green strength" characteristic and intermediate physical property profile of the prepolymers of this invention, a prepolymer of the nature more familiar to those skilled in the art was made to compare with Prepolymer I. The conventional prepolymer was prepared from 100.8 g (0.8064 molar equivalents) of 4,4'-diphenylmethane diisocyanate and 199.2 g (0.605 molar equivalents) of poly(tetramethylene) glycol having a molecular weight of 650. This provided a final molecular weight of a poly(tetramethylene) glycol weight percent of the conventional prepolymer approximating that of Prepolymer I.

The conventional prepolymer was synthesized in a manner similar to the procedure described in Example 1 prior to the addition of the chain extender. The final isocyanate value was found to be 2.62 percent. The prepolymer prepared in this manner was found to be a clear liquid of high viscosity. The conventional prepolymer is schematically illustrated as (X) in Figure 3 of the drawings.

To show the difference between the green strength of the conventional prepolymer and Prepolymer I, the following peel test procedure was used.

A heated sample of the prepolymers was obtained and then a film of each was made utilizing a draw-down bar having a fixed gap of 0.076 mm and casting a film directly onto a fabric of (1.7 ounce/yard) 57.6 g/m² Taffeta. A second layer of the Taffeta was immediately placed onto the cast film with even pressure applied to laminate the layers together in the nip between a metal and rubber rollers. One inch wide strips were then die cut and a peel test performed thereon within 10 minutes of casting the film. The conventional prepolymer required a peel force between (0.2 and 0.25 pounds) 0.9 and 1.1 N while Prepolymer I required a peel force or at least twice that of the conventional prepolymer. The failure mode in both cases was cohesive in nature.

**Example 2**

Several prepolymers, illustrative of the hydrophilic systems of this invention, were prepared from varying equivalents of 4,4'-diphenylmethane diisocyanate, different molecular weights polyoxyethylene glycol and hydroquinone di(2-hydroxyethyl)ether using the following procedure.
The flaked 4,4ʹ-diphenylmethane diisocyanate was charged to the reactor and allowed to melt under a dry purge by heating and stirring to 80 °C. The polyoxyethylene at 80 °C was added slowly over approximately 2 hours from a heated addition funnel to the stirred reaction vessel. The polyoxyethylene had been previously degassed at 100 °C under reduced pressure for approximately 2 hours. The theoretical percent isocyanate was reached generally within one hour after the final addition of polyoxyethylene as determined by a standard dibutylamine titration. The isocyanate-terminated polyoxyethylene so obtained was degassed under reduced pressure at this stage as the temperature was raised to 100 °C. With an increased nitrogen purge and stirring, the hydroquinone di(2-hydroxyethyl)ether was charged to the reaction at 100 °C. Immediately following the hydroquinone di(2-hydroxyethyl)ether addition, the reaction was raised to 125 °C. Beginning at this point, the product was degassed under reduced pressure. After the hydroquinone di(2-hydroxyethyl)ether addition, a viscosity increase was observed, and shortly thereafter opacity developed. As the product approached close to the theoretical isocyanate value, usually within one hour after the hydroquinone di(2-hydroxyethyl)ether addition, the warm, thick, opaque white prepolymer was discharged to a paint can blanketed with nitrogen, sealed and allowed to cool. Thereafter, the prepolymer was monitored for isocyanate value and found to be very stable over an extended period of time. The prepolymer prepared herein further exhibited stability by the retention of their processing characteristics and remained free of gel formation. Additionally, the prepolymer was characterised as shown below. As in Example 1, films were cast and then cured by ambient moisture.
<table>
<thead>
<tr>
<th></th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1,4'-diphenylmethane diisocyanate</strong>&lt;br&gt;Molar equivalents</td>
<td>1.774</td>
<td>11.55</td>
<td>3.434</td>
<td>1.540</td>
</tr>
<tr>
<td><strong>Poly oxyethylene</strong>&lt;br&gt;Molecular weight</td>
<td>1450</td>
<td>1000</td>
<td>1450</td>
<td>1450</td>
</tr>
<tr>
<td></td>
<td>0.887</td>
<td>5.78</td>
<td>1.72</td>
<td>0.770</td>
</tr>
<tr>
<td><strong>Hydroquinone di(2-hydroxyethyl)ether</strong>&lt;br&gt;Molar equivalents</td>
<td>0.452</td>
<td>2.89</td>
<td>0.430</td>
<td>0.514</td>
</tr>
</tbody>
</table>

**PROPERTIES OF PREPOLYTHERS**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Softening Point</strong>&lt;br&gt;(F/K)</td>
<td>77°C</td>
<td>102°C</td>
<td>23°C</td>
<td>95°C</td>
</tr>
<tr>
<td><strong>Melting Index</strong></td>
<td>7.68 g/10 minutes (2.16 kg at 77°C)</td>
<td>43.2 g/10 minutes (2.16 kg at 110°C)</td>
<td>77.5 g/10 minutes (2.16 kg at 110°C)</td>
<td>21.8 g/10 minutes (2.16 kg at 110°C)</td>
</tr>
<tr>
<td></td>
<td>66.6 g/10 minutes (5.00 kg at 77°C)</td>
<td>25.3 g/10 minutes (2.16 kg at 105°C)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**PROPERTIES OF CURR FILMS**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thickness</strong></td>
<td>0.06 - 0.37 mm</td>
<td>0.08 - 0.23 mm</td>
<td>0.16 - 0.27 mm</td>
<td>0.30 - 0.33 mm</td>
</tr>
<tr>
<td><strong>Tensile Strength at Break</strong>&lt;br&gt;(per ASTM D882-81)</td>
<td>(1900 psi) 13.1 MN/m²</td>
<td>(1800 psi) 12.4 MN/m²</td>
<td>(1400 psi) 9.65 MN/m²</td>
<td>(1900 psi) 13.1 MN/m²</td>
</tr>
<tr>
<td><strong>Elongation of Break</strong>&lt;br&gt;(per ASTM D882-81)</td>
<td>520 percent</td>
<td>720 percent</td>
<td>680 percent</td>
<td>960 percent</td>
</tr>
<tr>
<td><strong>Modulus of Elasticity</strong>&lt;br&gt;(per ASTM D882-81)</td>
<td>2200 psi 15.9 MN/m²</td>
<td>3100 psi 21.4 MN/m²</td>
<td>1200 psi 9.96 MN/m²</td>
<td>2300 psi 15.9 MN/m²</td>
</tr>
<tr>
<td><strong>Tear Strength</strong>&lt;br&gt;(per ASTM D1004-66)</td>
<td>(250 psi) 43.8 kN/m</td>
<td>(290 psi) 50.8 kN/m</td>
<td>(170 psi) 29.8 kN/m</td>
<td>(260 psi) 45.5 kN/m</td>
</tr>
<tr>
<td></td>
<td>(0.12 lb) 0.53N at 0.37mm</td>
<td>(0.16 lb) 2.05N at 0.83mm</td>
<td>(0.12 lb) 0.53N at 0.27mm</td>
<td>(1.6 lb) 7.12N at 0.30mm</td>
</tr>
</tbody>
</table>
| **Normalized HVR**<br>(g/m² - 24 hours - 2 mile) | 15300 | 7850 | 14200 | 16000 | (2 mile = 31 micrometres)
TABLE 3

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>IV</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Prepolymer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4'-diphenylmethane diisocyanate</td>
<td>3.434</td>
<td>1.774</td>
<td>1.540</td>
</tr>
<tr>
<td>Molar equivalents</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyoxyethylene (1450 molecular weight)</td>
<td>1.717</td>
<td>0.8870</td>
<td>0.7702</td>
</tr>
<tr>
<td>Molar equivalents</td>
<td>72.18</td>
<td>70.49</td>
<td>69.41</td>
</tr>
<tr>
<td>Weight percent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroquinone di(2-hydroxyethyl)ether</td>
<td>0.4300</td>
<td>0.4519</td>
<td>0.5135</td>
</tr>
<tr>
<td>Molar equivalents</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard Segments</td>
<td>8.8</td>
<td>11.5</td>
<td>22.50</td>
</tr>
<tr>
<td>Weight percent</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Properties of Cured Films**

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>IV</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>0.16 - 0.27 mm</td>
<td>0.06 - 0.37 mm</td>
<td>0.30 - 0.33 mm</td>
</tr>
<tr>
<td>Normalized MVTR (g/m² - 24 hours - 2 mils)</td>
<td>14200</td>
<td>15300</td>
<td>16000</td>
</tr>
<tr>
<td>(2 mils = 51 micrometres)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength at break</td>
<td>(1400 psi)</td>
<td>(1900 psi)</td>
<td>(1900 psi)</td>
</tr>
<tr>
<td>(per ASTM D882-81)</td>
<td>9.65 MN/m²</td>
<td>13.1 MN/m²</td>
<td>13.1 MN/m²</td>
</tr>
<tr>
<td>Elongation of Break</td>
<td>680 percent</td>
<td>520 percent</td>
<td>960 percent</td>
</tr>
<tr>
<td>(per ASTM D882-81)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>(1300 psi)</td>
<td>(2300 psi)</td>
<td>(2300 psi)</td>
</tr>
<tr>
<td>(per ASTM D882-81)</td>
<td>8.96 MN/m²</td>
<td>15.9 MN/m²</td>
<td>15.9 MN/m²</td>
</tr>
<tr>
<td>Tear strength</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initiation (per ASTM D1004-66)</td>
<td>(170 p1i)</td>
<td>(250 p1i)</td>
<td>(260 p1i)</td>
</tr>
<tr>
<td>Propagation (per ASTM D1938-67)</td>
<td>0.121b</td>
<td>0.53N at 0.27 mm</td>
<td>43.8 kN/m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.37N at 0.37 mm</td>
<td>(260 p1i) 45.5 kN/m</td>
</tr>
</tbody>
</table>

and subsequent film from Example 2, were synthesized containing essentially the same weight percent polyoxyethylene while varying the phase-separating hard segment concentration. The data in Table 3 show the simultaneous improvement in physical properties and MVTR with improved phase separation.
Comparative Example 2

A prepolymer (Prepolymer VIIA) was prepared from 96.1 g (0.769 molar equivalents) of 4,4'-diphenylmethane diisocyanate, 277.3 g (0.384 molar equivalents) of poly(oxyethylene) glycol having a molecular weight of 1450, and 26.56 g (0.1922 molar equivalents) of 1,2-bis(2-aminophenylthio)ethane using the following method.

Flaked 4,4'-diphenylmethane diisocyanate was charged to a 1000 ml reactor and allowed to melt under a dry nitrogen purge, by heating and stirring to 80 °C. Poly(oxyethylene) glycol at 80 °C was slowly added, with stirring, to the diisocyanate from an addition funnel over a 2 hour period. The poly(oxyethylene) glycol had previously been degassed at 95 °C for 2 hours under reduced pressure. After 60 minutes the free isocyanate was found to be 4.32 percent.

The temperature of the isocyanate-capped poly(oxyethylene) glycol formed by the first step was raised to 100 °C. 26.56 g of flaked, 1,2-bis(2-aminophenylthio)-ethane were charged to the reactor. Vigorous stirring and a nitrogen purge was maintained during this step. Immediately the prepolymer changed from colorless to a translucent yellow. In the following fifteen minutes the prepolymer had increased in viscosity. Twenty minutes after the addition of 1,2-bis(2-aminophenylthio)-ethane, the prepolymer was discharged into paint cans, blanketed with nitrogen and sealed. Samples were taken for free isocyanate titrations. At this point, the prepolymer was of high viscosity, a translucent yellow and the free isocyanate was later found to be 2.02 percent. At this point, to avoid undue heat treatment, films were cast and cured for characterization as shown in Table 4A.

Packaged Prepolymer VIIA was found to have stable isocyanate value and remain workable for at least several days. The physical properties of Prepolymer VIIA were unexpectedly low for urea hard segments. This and the lack of opacity in the prepolymer raised questions as to the suitableness of this hard segment in this system, and these results are presently not fully understood.

### TABLE 4A

<table>
<thead>
<tr>
<th>PROPERTIES OF PREPOLYMER VIIA</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening Point (TMA)</td>
<td>27 °C</td>
</tr>
<tr>
<td>Melting Index:</td>
<td></td>
</tr>
<tr>
<td>2.16 kg at 50 °C</td>
<td>25.3 g/10 minutes</td>
</tr>
<tr>
<td>2.16 kg at 60 °C</td>
<td>46.8 g/10 minutes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PHYSICAL PROPERTIES OF A CURED FILM OF PREPOLYMER VIIA</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>0.22 - 0.26 mm</td>
</tr>
<tr>
<td>Tensile Strength at Break (per ASTM D882-81)</td>
<td>(590 psi) 4.07 MN/m²</td>
</tr>
<tr>
<td>Elongation at Break (per ASTM D882-81)</td>
<td>410 percent</td>
</tr>
<tr>
<td>Modulus of Elasticity (per ASTM D882-81)</td>
<td>(710 psi) 4.90 MN/m²</td>
</tr>
<tr>
<td>Tear Strength</td>
<td></td>
</tr>
<tr>
<td>Initiation (per ASTM D1004-86)</td>
<td>(100 ppi) 17.5 kN/m</td>
</tr>
<tr>
<td>Propagation (per ASTM D1938-67)</td>
<td>(0.02 lb) 0.09 N at 0.22 mm</td>
</tr>
</tbody>
</table>

Example 4

A prepolymer (Prepolymer VIIIB) of this invention was prepared from 91.90 g (0.7352 molar equivalents) of 4,4'-diphenylmethane diisocyanate, 182.8 g (0.3679 molar equivalents) of poly(oxytetramethylene) glycol having a molecular weight of 1000 and 25.37 g (0.1836 molar equivalents) of 1,2-bis(2-aminophenylthio)-ethane.

To a 1000 ml reactor equipped with a stirrer and nitrogen purge, the 4,4'-diphenylmethane diisocyanate was charged in solid form. With the nitrogen purging, the temperature of the reactor was raised to 80 °C. When the diisocyanate had melted, the poly(oxytetramethylene) glycol was slowly added via an addition funnel over a 50 minute period. The poly(oxytetramethylene) glycol had been previously degassed at 95 °C under reduced pressure. After an additional 45 minutes, the free isocyanate value was found to be 5.3 percent.
The temperature of the reactor was raised to 100 °C and the 1,2-bis(2-aminophenylthio)-ethane added all at once in solid form. After 15 minutes, the prepolymer had turned from colorless to a translucent yellow. At this time, the prepolymer was poured into paint cans and sealed under nitrogen. A titration sample taken at this time had a free isocyanate value of 2.3 percent. It was found to be important to pour the prepolymer immediately after the 1,2-bis(2-aminophenylthio)-ethane had reacted to prevent an undue increase in viscosity. The rapid increase in viscosity is thought to be due to biuret formation occurring at high temperatures. To avoid undue heat treatment, films were cast at this point and cured for characterization as shown in Table 4B.

**TABLE 4B**

<table>
<thead>
<tr>
<th>PROPERTIES OF PREPOLYMER VIIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening Point (TMA)</td>
</tr>
<tr>
<td>Melting Index:</td>
</tr>
<tr>
<td>2.16 kg at 50 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PHYSICAL PROPERTIES OF A CURED FILM OF PREPOLYMER VIIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Tensile Strength at Break</td>
</tr>
<tr>
<td>Elongation at Break (per ASTM D882-81)</td>
</tr>
<tr>
<td>Modulus of Elasticity (per ASTM D882-81)</td>
</tr>
<tr>
<td>Tear Strength</td>
</tr>
<tr>
<td>Initiation (per ASTM D1004-86)</td>
</tr>
<tr>
<td>Propagation (per ASTM D1938-67)</td>
</tr>
</tbody>
</table>

**Example 5**

Prepolymer I provided a successful solvent-free adhesive for lamination of a textile and a plastic film utilizing a conventional, direct gravure printer. A dot pattern of Prepolymer I was metered onto an expanded PTFE membrane, product designation PN 11124NA, available from W.L. Gore & Associates, Inc., by a gravure roller in such a manner as to provide coverage of approximately 50 percent of the membrane. The gravure roller was heated to 120 °C and was found to provide a laydown of about (5.5 g/yd²) 4.6 g/m². The membrane was held against the gravure roller by a low durometer rubber roller at a pressure sufficient to effect removal of the adhesive dots onto the membrane. The printed membrane was transported at (75 fpm) 22.9 m/min for a distance of about (18 inches) 45.72 cm and laminated to a (3.0 ounce/yard) 102 g/m² Taslan (Registered Trade Mark) fabric in a nip between a chrome roller heated to 100 °C and a low durometer rubber roller. The phase-separation that had occurred in the prepolymer prevented wicking of the adhesive into the textile. Its softness provided good wetting characteristics. The laminated product was wound onto a core and allowed to cure with ambient moisture. Subsequently, the entire laminate was treated with a water repellent treatment in a standard process.

The laminate thus formed was found to have good hand characteristics due to the controlled adhesive penetration provided by the phase-separation characteristics. The adhesive provided excellent durability as the textile and membrane laminate did not delaminate in over 1500 continuous hours of an ambient-temperature water agitation in a Maytag washer.

**Comparative Example 3**

The following example illustrates the situation wherein a non-suitable hard segment is obtained, the prepolymer being outside the scope of this invention.

Using a procedure similar to that described in Example 1, but replacing the 1,4-butanediol there used with 10.14 g (0.1950 molar equivalents) neopentyl glycol and using 97.65 g (0.7892 molar equivalents) 4,4'-diphenylmethane disiocyanate and 192.21 g (0.3906 molar equivalents) of poly(oxytetramethylene) glycol of molecular weight 1000, there was prepared a prepolymer containing a non-suitable hard segment.
The prepolymer was observed to be a clear high-viscosity liquid at room temperature. Furthermore, stored at room temperature the isocyanate value dropped from 2.86 percent isocyanate to 1.34 percent isocyanate in 7 days, illustrating poor shelf stability.

Comparative Example 4

An attempt was made to prepare a prepolymer outside of the limitation of equation (b) above by the reaction of 176.34 g (1.41 molar equivalents) 4,4’-diphenylmethane diisocyanate, 252 g (0.3527 molar equivalents) polyoxyethylene of molecular weight 1450 and 71.67 g (0.7054 molar equivalents) hydroquinone di(2-hydroxyethyl) ether by a procedure similar to that described in Example 3. Within 30 minutes after the addition of the hydroquinone di(2-hydroxyethyl)ether the prepolymer had essentially gelled and was found to have an isocyanate value of 1.45 percent, well below the theoretical value of 2.96 per cent isocyanate.

A second attempt at preparing this polymer was made wherein the prepolymer was removed from the reactor 15 minutes after the hydroquinone di(2-hydroxyethyl)ether was added. At this stage the prepolymer was an opaque white, of uniform paste viscosity and was found to have an isocyanate value of 4.8 percent, well above the theoretical value. However, the next day the isocyanate value had dropped dramatically to 1.7 percent. It is believed that the formation of allophanate linkages is the explanation for these poor results.

Example 6

A prepolymer (Prepolymer VIII) of this invention was prepared from 146.9 g (1.175 molar equivalents) of 4,4’-diphenylmethane diisocyanate, 339.9 g (0.5877 molar equivalents) of 1200 molecular weight polyoxypropylene glycol and 13.20 g (0.2933 molar equivalents) of 1,4-butanediol using the following procedure.

Liquid 4,4’-diphenylmethane diisocyanate was charged to a reactor heated to 80 °C and purged with dry nitrogen. From a jacketed addition funnel, polyoxypropylene glycol at 77 °C was rapidly added to the diisocyanate with stirring. After 3 hours, the free isocyanate was found to be 4.8 percent.

The 1,4-butanediol at room temperature was added in one charge to the isocyanate-capped polyoxypropylene glycol formed in the first step. After 1.5 hours, the prepolymer turned from colorless to white, and the free isocyanate was found to be 2.3 percent.

The resulting prepolymer was poured warm from the reactor into paint cans, blanketed with nitrogen, and sealed. Characteristics of the prepolymer and films cast therefrom are shown below.

**TABLE 5**

<table>
<thead>
<tr>
<th>PROPERTIES OF PREPOLYMER VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softening Point (TMA)</td>
</tr>
<tr>
<td>Melting Index:</td>
</tr>
<tr>
<td>2.16 kg at 35 °C</td>
</tr>
<tr>
<td>2.16 kg at 45 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PHYSICAL PROPERTIES OF A CURED FILM OF PREPOLYMER VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Elongation at Break (per ASTM D882-81)</td>
</tr>
<tr>
<td>Modulus of Elasticity (per ASTM D882-81)</td>
</tr>
<tr>
<td>Tear Strength</td>
</tr>
<tr>
<td>Initiation (per ASTM D1004-66)</td>
</tr>
<tr>
<td>Propagation (per ASTM D1938-67)</td>
</tr>
</tbody>
</table>

Example 7

A coated textile was prepared according to the procedure illustrated in Figure 2. The prepolymer of choice was preheated to about 110 °C and placed into the puddle 6 created by a doctor blade 8 affixed at a
gap of approximately (2 mils) 51 micrometers from the FEP belt 2. The blade was heated to about 120 °C, and the belt was heated to approximately 90 °C as it ran in contact with the heated roller 4 maintained at about 120 °C. The prepolymer was shaped into a film 10 by the doctor blade onto the belt and allowed to cool as the belt ran against the chilled roller 12 maintained at 0-10 °C. The phase-separated prepolymer film was then laminated to the textile fabric 14 at the nip between rollers 12 and 16. The coated textile composite 18 was released from the belt as it was pulled over peel bar 20 to define the angle of release, approximately 90 °C. The coated textile was then rolled up with release paper and allowed to cure. In this example, the coated textile made with Prepolymer V was subsequently treated on the textile side with a fluorocarbon water repellant treatment. The coated textiles were characterized as shown in Table 6 below.

<table>
<thead>
<tr>
<th>PREPOLYMER</th>
<th>III</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>TASLAN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight</td>
<td>(3 ounces/yard) 102 g/m²</td>
<td>(3 ounces/yard) 102 g/m²</td>
</tr>
<tr>
<td>Thickness</td>
<td>(9.0 miles) 229 micrometers</td>
<td>(9.0 miles) 229 micrometers</td>
</tr>
<tr>
<td>MVTR (g/m² • 24 hours)</td>
<td>15300</td>
<td>15300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COATED TASLAN</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Thickness (mils)</td>
<td>(11.4) 290 micrometers</td>
<td>(12.4) 315 micrometers</td>
</tr>
<tr>
<td>MVTR (g/m² • 24 hours)</td>
<td>3230</td>
<td>3530</td>
</tr>
<tr>
<td>WEP (Water Entry Pressure) (psi per Federal Standard 191, Method 5512)</td>
<td>(121) 834 kN/m²</td>
<td>(191) 317 kN/m²</td>
</tr>
<tr>
<td>Abrasion (cycles)</td>
<td>&gt;4000</td>
<td>&gt;4000</td>
</tr>
</tbody>
</table>

In addition, the coated product was found to be durably waterproof under scoring and flexing tests. As such, this coated product would provide an excellent rain protective wear.

Example 8

A layered article as disclosed in U.S. Patent 4,194,041 was made from Prepolymer IV above and an expanded PTFE membrane, product designation PN 11124NA, available from W.L.Gore & Associates, Incorporated having a Gurley number of about 5 seconds, bubble point of about (23 psi) 158 kN/m², thickness of about 38 mm and a weight of about 10 g/m².

A three-roller assembly was employed, all rollers heated to 95 °C and Prepolymer IV was heated to 95 °C. A continuous film of uniform thickness of Prepolymer IV was formed on the middle roller via the padder formed at the nip between the first roller and the second roller. In this case, the first roller was a gravure roller, and the second roller, a rubber roller. Hydraulic pressure generated between the rubber roller and the backing roller was adjusted to drive the prepolymer into the matrix of the expanded PTFE membrane being fed into the coater at (20 fpm) 6.1 m/min.

The composite was rolled up with release paper and allowed to cure in ambient air.

The layered article was laminated to a (3 ounce/yard²) 102 g/m² Taslan fabric by adhesive applied in a dot pattern so as not to occlude more than half of the membrane surface area. The layered article was laminated so as to expose the cured Prepolymer IV face. The laminate was characterized as shown in Table 7.

<table>
<thead>
<tr>
<th>LAYERED ARTICLE LAMINATE</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>prepolymer II Laydown</td>
<td>18 g/m²</td>
</tr>
<tr>
<td>Expanded PTFE Membrane</td>
<td>18 g/m²</td>
</tr>
<tr>
<td>MVTR (g/m² • 24 hours)</td>
<td>10,755</td>
</tr>
<tr>
<td>Abrasion (cycles)</td>
<td>1500</td>
</tr>
</tbody>
</table>
The laminate was further found to be highly durable to flexing and scoring. As such, this laminate would provide excellent rain protective wear.

Example 9

Prepolymer I was found to be effective as a sealant when applied in the molten state to a raw material leak at a hole between a metal pipe and a steel drum. The phase-separation allowed the prepolymer to instantly set up and then subsequently cure with ambient moisture. The sealant proved effective.

Example 10

To illustrate further the versatility of the prepolymer of this invention, a flat electrical-cable-jacketing formation was found to be enhanced in its physical properties, particularly tear strength, when a small amount of Prepolymer I was incorporated. Prepolymer I provided characteristics, particularly its low melt temperature, that allowed easy processing in an already existent formulation. Samples of the cable jacketing material were prepared with and without Prepolymer I in accordance with Table 8. The compounds were mixed on a two-roller, (9" x 18") 23 cm x 46 cm mill in two stages.

Stage one consisted of combining ingredients numbered 1 through 5 of Table 8 on the mill at a temperature between 20 °C and 100 °C. When the mixing was deemed to be complete, i.e. complete incorporation and dispersion of the ingredients, the material was removed from the mill as a sheet and allowed to cool below 50 °C. The mill was subsequently allowed to cool to below 50 °C.

Stage two consisted of returning the cooled sheet from stage 1 to the cooled mill and subsequently adding ingredients 6 through 9 of Table 8 and allowing the ingredients to be incorporated into the rubber mix.

The mill temperature during this process stage was maintained in the range of 20 °C and 80 °C.

The sheet was removed from the mill and subsequently molded into sheets of 0.5 to 3 mm thickness at a pressure between (500 pounds per square inch) 3.45 MN/m² and (2000 pounds per square inch) 13.79 MN/m² between the heated platen of a hydraulic press. The temperature of the platen was maintained at 180 °C throughout the molding time of 30 minutes. After 30 minutes the mold was depressurized, the molded sheet removed and the sheet allowed to cool to a temperature of 20 plus or minus 3 °C for a minimum of 16 hours. The samples were characterized as shown in Table 8.

| TABLE 8 |
|-----------------|----------|----------|
| **ALL PARTS BY WEIGHT** | **Sample A** | **Sample B** |
| 1. Ethylene Acrylic Resin | 100 | 100 |
| 2. Ethylene Vinyl Acetate Resin | 15 | 15 |
| 3. Prepolymer I | - | 10 |
| 4. Alumina Trihydrate | 150 | 150 |
| 5. Associated Stabilizers, Processing Aids | 6.5 | 6.5 |
| 6. Diphenyl Guanidine | 2.5 | 2.5 |
| 7. Hexamethylene Diamine Carbamate | 1.25 | 1.25 |
| 8. Dicumyl Peroxide | 3 | 3 |
| 9. Associated Stabilizers, Processing Aids | 11 | 11 |
| **PHYSICAL PROPERTIES CABLE JACKETING** | | |
| Tensile Strength (per ASTM D882-81) | (1400 psi) 9.65 MN/m² | (1400 psi) 9.65 MN/m² |
| Elongation at Break (per ASTM D882-81) | 170 percent | 293 percent |
| Tear Strength (per ASTM D1004-66) | (22 pli) 3.65 kN/m | (37 pli) 6.48 kN/m |

Claims

1. A reactive polymer system being an opaque solid at room temperature and having a two-phase morphology comprising a reactive, segmented, polyether polyurethane prepolymer, said prepolymer comprising the reaction product of
(i) a poly (alkylene ether) polyl having a number average molecular weight of from 600 to 3500 and having a functionality of at least 2;
(ii) an organic isocyanate having a functionality of at least 2; and
(iii) a low molecular weight chain extender having a molecular weight lower than 500 and having a functionality of at least 2;
wherein the reactants are employed in such proportions so as to satisfy the following equations:

\[
\frac{\text{Eq}_{\text{NCO}}}{\text{Eq}_{\text{OH}} + \text{Eq}_{\text{CE}}} \geq 1.1
\]

(b) \(\text{Eq}_{\text{OH}} \geq \text{Eq}_{\text{CE}}\)
(c) \(\text{Eq}_{\text{CE}} > 0\),

wherein \(\text{Eq}_{\text{NCO}}\) denotes the equivalents of the isocyanate employed and \(\text{Eq}_{\text{OH}}\) and \(\text{Eq}_{\text{CE}}\) denote the respective molar equivalents of the polyl and chain extender employed; and wherein the reaction product of the isocyanate and chain extender provides hard segments and the polyl provides soft segments, said hard segments being incompatible with said soft segments;
the reactive polymer system having a two phase morphology with a hard segment phase comprising domains of the hard segments of the prepolymer and a soft segment phase comprising domains of the soft segments of the prepolymer and whereby the hard segment phase is dispersed within the soft segment phase.

2. A reactive polymer system according to claim 1 wherein the polyl has a functionality of 2.
3. A reactive polymer system according to claim 1 or 2 wherein the isocyanate has a functionality of 2.
4. A reactive polymer system according to any of the claims 1 to 3 wherein the chain extender has a functionality of 2.
5. A reactive polymer system according to any of the claims 1 to 4 wherein the polyl is selected from poly (tetramethylene ether) and poly (ethylene ether).
6. A reactive polymer system according to any of the claims 1 to 5 wherein the isocyanate is 4,4' diphenylmethane diisocyanate.
7. Use of the reactive polymer system according to any of the claims 1 to 6 as an adhesive.
8. Use of the reactive polymer system according to any of the claims 1 to 6 in making a coated substrate.
9. Use of the reactive polymer system according to any of the claims 1 to 6 for sealing.
10. Use of the reactive polymer system according to claims 1 to 6 in electrical cable jackets.
11. A product produced by curing the reactive polymer system according to any of the claims 1 to 6.
12. A product according to claim 11 in the form of a film with a moisture vapour transmission rate exceeding 5000 g/m² • 24 h • 50,8 µm.

Patentansprüche

1. Reaktives Polymersystem, das bei Raumtemperatur ein undurchsichtiger Feststoff ist und eine Zwei-
phasenmorphologie hat, das ein reaktives, aus Segmenten bestehendes Polyether-, Polyurethan-
Vorpolymerisat umfaßt, wobei dieses Vorpolymerisat das Reaktionsprodukt von
(i) einem Poly(alkylenether)polyol mit einem Zahlenmittel des Molekulargewichtes von 600 bis 3500
und einer Funktionalität von mindestens 2;
(ii) einem organischen Isocyanat mit einer Funktionalität von mindestens 2; und
(iii) einem Kettenverlängerungsmittel mit geringem Molekulargewicht umfaßt, das ein Molekulargewicht im Bereich von weniger als 500 und eine Funktionalität von mindestens 2 aufweist, wobei die Reaktanten in solchen Verhältnissen eingesetzt werden, das die folgenden Gleichungen erfüllt werden:

\[
\frac{\hat{\text{Aqu}} \cdot \text{NCO}}{\hat{\text{Aqu}} \cdot \text{OH} + \hat{\text{Aqu}} \cdot \text{CE}} \geq 1,1
\]

(b) \( \hat{\text{Aqu}} \cdot \text{OH} \geq \hat{\text{Aqu}} \cdot \text{CE} \)

(c) \( \hat{\text{Aqu}} \cdot \text{CE} > 0 \)

wurin \( \hat{\text{Aqu}} \cdot \text{NCO} \) die verwendeten \( \hat{\text{Aquivalente}} \) des Isocyanats bedeutet und \( \hat{\text{Aqu}} \cdot \text{OH} \) und \( \hat{\text{Aqu}} \cdot \text{CE} \) die entsprechenden verwendeten molaren \( \hat{\text{Aquivalente}} \) des Polyols und des Kettenverlängerungsmittels sind; wobei das Reaktionsprodukt des Isocyanats und des Kettenverlängerungsmittels die harten Segmente liefert und das Polyol die weichen Segmente, wobei die harten Segmente mit den weichen Segmenten nicht kompatibel sind; wobei das reaktive Polymersystem eine Zweiphasenmorphologie mit einer Phase der harten Segmente, die Bereiche der harten Segmente des Vorpolymersats umfaßt, und einer Phase der weichen Segmente aufweist, die Bereiche der weichen Segmente des Vorpolymersats umfaßt, wobei die Phase der harten Segmente in der Phase der weichen Segmente dispergiert ist.

2. Reaktives Polymersystem nach Anspruch 1, worin das Polyol eine Funktionalität von 2 aufweist.

3. Reaktives Polymersystem nach Anspruch 1 oder 2, worin das Isocyanat eine Funktionalität von 2 aufweist.

4. Reaktives Polymersystem nach einem der Ansprüche 1 bis 3, worin das Kettenverlängerungsmittel eine Funktionalität von 2 aufweist.

5. Reaktives Polymersystem nach einem der Ansprüche 1 bis 4, worin das Polyol aus Poly-(tetramethylenether) und Poly(ethylenether) ausgewählt ist.

6. Reaktives Polymersystem nach einem der Ansprüche 1 bis 5, worin das Isocyanat 4,4'-Diphenylmethan-disocyanat ist.

7. Verwendung des reaktiven Polymersystems nach einem der Ansprüche 1 bis 6 als Klebstoff.

8. Verwendung des reaktiven Polymersystems nach einem der Ansprüche 1 bis 6 bei der Herstellung eines beschichteten Substrats.

9. Verwendung des reaktiven Polymersystems nach einem der Ansprüche 1 bis 6 zum Abdichten.

10. Verwendung des reaktiven Polymersystems nach einem der Ansprüche 1 bis 6 bei Ummantelungen für elektrische Kabel.

11. Produkt, das durch Härten des reaktiven Polymersystems nach einem der Ansprüche 1 bis 6 erhalten wurde.

12. Produkt nach Anspruch 11 in Form eines Films mit einer Wasserdampfdurchlässigkeit von mehr als 5000 g/m² * 24 h * 50,8 µm.
Recommandations

1. Système polymère réactif, consistant en un solide opaque à la température ambiante, et ayant une morphologie biphasique comprenant un prépolymère de polyéther-polyuréthane segmenté réactif, ce prépolymère comprenant le produit de réaction :
   (i) d'un poly(éther d'alkylène) polyol ayant un poids moléculaire moyen en nombre de 600 à 3 500 et ayant une fonctionnalité d'au moins 2 ;
   (ii) d'un isocyanate organique ayant une fonctionnalité d'au moins 2 ; et
   (iii) d'un agent d'extension de chaîne de faible poids moléculaire ayant un poids moléculaire inférieur à 500 et ayant une fonctionnalité d'au moins 2 ; dans lequel les réactifs sont employés selon des proportions appropriées pour satisfaire les équations suivantes :
   (a) \[
   \frac{\text{Eq}_{\text{NCO}}}{\text{Eq}_{\text{OH}} + \text{Eq}_{\text{CE}}} \geq 1.1
   \]
   (b) \text{Eq}_{\text{OH}} \geq \text{Eq}_{\text{CE}}
   (c) \text{Eq}_{\text{CE}} > 0,
   dans lesquelles \text{Eq}_{\text{NCO}} représente le nombre d'équivalents de l'isocyanate employé et \text{Eq}_{\text{OH}}, ainsi que \text{Eq}_{\text{CE}} représentent les nombres d'équivalents molaires respectifs du polyol et de l'agent d'extension de chaîne employés ; et dans lequel le produit de réaction de l'isocyanate et de l'agent d'extension de chaîne, procure des segments durs, et le polyol procure des segments mous, ces segments durs étant incompatibles avec les segments mous ;
   le système de polymère réactif ayant une morphologie biphasique comprenant une phase de segments durs comprenant les domaines des segments durs du prépolymère et une phase de segments mous comprenant les domaines des segments mous du prépolymère, et la phase de segments durs étant dispersée dans la phase de segments mous.

2. Système polymère réactif selon la recommandation 1, dans lequel le polyol a une fonctionnalité de 2.

3. Système polymère réactif selon la recommandation 1 ou 2, dans lequel l'isocyanate a une fonctionnalité de 2.

4. Système polymère réactif selon l'une quelconque des recommandations 1 à 3, dans lequel l'agent d'extension de chaîne a une fonctionnalité de 2.

5. Système polymère réactif selon l'une quelconque des recommandations 1 à 4, dans lequel le polyol est choisi parmi le polyéther de tétraméthylène et le polyéther d'éthylène.

6. Système polymère réactif selon l'une quelconque des recommandations 1 à 5, dans lequel l'isocyanate est le 4,4'-diphényliméthane disocyanate.

7. Utilisation du système polymère réactif selon l'une quelconque des recommandations 1 à 6, comme adhésif.

8. Utilisation du système polymère réactif selon l'une quelconque des recommandations 1 à 6, pour fabriquer un substrat revêtu.

9. Utilisation du système polymère réactif selon l'une quelconque des recommandations 1 à 6, pour effectuer un étanchement.

10. Utilisation du système polymère réactif selon l'une quelconque des recommandations 1 à 6, dans des gaines de câble électrique.

12. Produit selon la revendication 11, sous la forme d'un film ayant une vitesse de transmission de vapeur d'humidité supérieure à 5 000 g/m²·24 heures, 50.8 µm.
(VI)

(VII)

(VIII)

(IX)

HO–(Ro)_{r}–H (X)

(XI)

Fig. 3b.