Description

This invention relates to the halogenation of the surfaces of polymers, particularly polymeric molded articles to improve resistance to various acids and solvents.

Crosslinked (thermoset) polymers of strained ring polycyclic cycloolefins are extensively used for making molded structural articles. The preparation of these polymers, usually based on dicyclopentadiene, is known, for example, from U.S. Patent 4,400,340, which describes a reaction injection molding (RIM) technique in which a stream containing a monomer to be polymerized and the metathesis catalyst and a second stream containing a catalyst activator and additional monomer are brought together in a mixing head and substantially immediately injected into a mold where the monomer polymerizes within seconds to form a shaped article matching the shape of the mold. Details of the catalyst preparation are well known, for instance from U.S. Patent 4,568,660. The polymerization is effected by the opening of a cycloolefin ring, and the monomers are described as being metathesis-polymerizable. The reaction is catalyzed by a transition metal catalyst such as a tungsten or molybdenum salt, preferably tungsten halide or tungsten oxyhalide, activated by an alkyl aluminum compound. The gelation stage of the reaction, unless modified to delay it, takes place almost instantaneously. Such polymers can also be molded from a single stream with use of an additive to delay gelation.

These polymers and other thermoset polymers, because they are extensively crosslinked, are characterized by high impact strength, high flexural modulus, insolubility in common solvents such as gasoline, naphtha, chlorinated hydrocarbons, and aromatics, and resistance to flow at elevated temperatures.

Although insoluble, the thermoset polymers are still subject to appreciable swelling in solvents and degradation by acids, and when immersed in hydrocarbon solvents for a prolonged period, will absorb the hydrocarbons to an extent sufficient to cause blistering and swelling and degrade the polymer's properties. Another undesirable feature of these polymers is that when polymerization of the monomer has been completed, there is often a small percentage of monomer remaining in the article, which is slowly emitted over a period of time.

U.S. Pat. No. 3,758,450 discloses a process for eliminating easily hydrolysable groups from the surfaces of fluorinated hydrocarbon elastomeric articles to increase the thermal stability and hydrolytic resistance of the articles. This process uses fluorine diluted with an inert gas at an elevated temperature with a contact time of a few seconds.

There is a need for a method for treating surfaces of thermoset polymer articles made from strained ring cycloolefins to increase their resistance to degradation by chemicals such as acids, hydrocarbons, and other materials, and to reduce the emission of residual monomer remaining in the article after polymerization, as well as to improve the adherence of paints to the surfaces of such articles.

According to the invention, a method for treating surfaces of strained ring cycloolefin polymer articles comprises halogenating the surfaces of said articles with a halogen, a pseudohalogen compound, or an interhalogen compound.

The properties of polycyclic cycloolefin articles such as those containing poly(dicyclopentadiene) can be substantially improved by halogenation of the article's surface according to the invention. Both aqueous and gaseous treatments of the polymer have been found to significantly improve the resistance to various acids and solvents. Chlorine, fluorine and bromine, in particular, when incorporated into the surface of the polymer, increase chemical resistance, improve retention of properties upon aging, reduce emission of residual monomer, and encourage better adhesion of paint.

For instance, halogenating agents that provide the desired chemical resistance on the polymer surface include dry chlorine gas, aqueous chlorine, liquid bromine, aqueous bromine, and fluorine gas. Treatment with iodine changed the polymer from an insulator to a semiconductor. These halogens probably attach at the polymer's double bonds.

Similar enhancement of surface properties can be obtained through treatments with compounds that are well known to the skilled man to react in the same way as halogens, e.g., pseudohalogens and interhalogen compounds. Those compounds, like halogens, add to the surface of the polymer through exposure of the surface of the polymer according to the invention, by addition to double or triple bonds or substitution in aromatic rings. The pseudohalogen compounds include ClSCN, ISCN, INCO, $(SCN)_2$, IN_3, INO_3, and BrN_3. The interhalogen compounds include ICl, IF, and BrF.

Preferably, the polymer halogenated according to the invention (which is the polymer used in the examples below), is polydicyclopentadiene (DCPD). It will be clear to the skilled man that other strained ring cycloolefins will have the same surface characteristics in the context of the invention: therefore, higher cyclopentadiene oligomers, norbornene, norbornadiene, 4-alkylidene norbornenes, dimethanooctahydronaphthalene, dimethanohexahydronaphthalene and substituted derivatives of these compounds may

be used and are interchangeable with all or part of the (DCPD) in the examples.

The preferred cyclic olefin monomer is dicyclopentadiene or a mixture of (DCPD) with other strained ring hydrocarbons. If a mixture of two monomers is used, either monomer may constitute 1 to 99 mole % of the mixture, which is preferably about 75 to 99 mole % of dicyclopentadiene.

The following Examples further illustrate the invention. Two different DCPD containing polymers (labeled Polymer 1 and Polymer 2) were subjected to the surface treatments. Polymer 1 contained a small amount of tricyclopentadiene and Polymer 2 contained about 11 weight % tricyclopentadiene. Each of the polymers were made with a molar ratio of 1000:0.56:1.68 of monomer: tungsten catalyst: aluminum activator (85:15 trioctylaluminum: dioctylaluminum iodide). One equivalent dichlorodiphenylmethane was added to the catalyst for each equivalent of the tungsten catalyst. One equivalent of diglyme was added for each equivalent of aluminum activator. Table 1 details the composition of these polymers. The remainder of each composition to a 100 weight % total is made up of DCPD. Irganox 1035, a stabilizer, is thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy) hydrocinnamate manufactured by Ciba-Geigy.

TABLE 1

Polymer 1	
Weight %	Ingredient
3.0	Tricyclopentadiene
4.5	EPDM rubber (Ethylene-propylene-termonomer)
0.7	Diphenylamine
1.3	Irganox 1035
0.2	Carbon black
Polymer 2	
Weight %	Ingredient
11.0	Tricyclopentadiene
5.0	EPDM rubber
0.7	Diphenylamine
1.3	Irganox 1035

The effect of the surface modification was tested in several ways. Most reactions were run on polymer samples 4x4 mm square cut from 3.2 mm (1/8 inch) thick sheets. Those samples that were to be tested for the rate of loss of residual DCPD by gas chromatography were 0.85 x 3.75 cm strips. After each treatment was completed, the samples were cooled, rinsed well with water, dried and weighed. The infrared spectra were taken of the molded surfaces. These samples fitted the holder for measurement of the infrared spectrum in the range from 4000 to 600 cm^{-1} by the photoacoustic method. The depth of penetration included the top 17 microns of the polymer at 1735 cm^{-1}, the top 18 microns at 1450 cm^{-1} and the top 24 microns at 800 cm^{-1}. Attenuated total reflectance infrared spectroscopy penetrates 1 to 2 microns, also varying with the same wavelengths as listed above. These measurements are commonly used in the surface characterization of polymers. The infrared spectrum of the untreated polymer exhibits the following peaks: cis cyclopentene stretch at 3048 cm^{-1} cis norbornene stretch at 3048 cm^{-1}, cis/trans double bond linear stretch at 3005 cm^{-1}, trans double bond stretch at 1665 cm^{-1}, cis double bond stretch at 1653 cm^{-1}, cis cyclopentene stretch at 1618 cm^{-1}, cis norbornene stretch at 1570-1590 cm^{-1}, cis linear double bond in plane deformation at 1412 cm^{-1}, trans linear double bond out of plane deformation at 975 cm^{-1}, cis cyclopentene in plane deformation at 945 cm^{-1}, cis linear double bond out of plane deformation at 753 cm^{-1}, cis cyclopentene out of plane deformation at 733 cm^{-1} and 712 cm^{-1} and cis norbornene out of plane deformation at 700 cm^{-1}. Most of the interpretation was based on the bands at 3048 cm^{-1} and 975 cm^{-1}. Traces of hydroxyl bands were difficult to eliminate even with drying in a desiccator and with desiccant in the instrument. Data on solvent and acid resistance of the polymers are in the discussion with the examples. The times given for the reaction are usually the minimum time for the reaction to go to completion.

EXAMPLE 1

In Example 1 dicyclopentadiene polymers and copolymers were treated with dry chlorine gas at 90 °C. for 20 hours. A 0.5 x 2.5 inch strip cut from a 1/8 inch thick plaque of polymer 1 was placed in a three neck round bottom flask heated in an oil bath. A slow stream of chlorine from a cylinder was passed in through a tube and out an exit bubbler. After 20 hours at 90 °C., the strip was removed, washed well with water and dried in an open dish. Analysis of the surface by photoacoustic infrared spectroscopy showed strong new absorption at 1350-650 cm^{-1} with 1272 cm^{-1} assigned to CHCl and 850-680 cm^{-1} assigned to CCl. No band due to a double bond remained at 3048 cm^{-1} indicating the addition of chlorine to the double bond as shown by the disappearance of the 3048 cm^{-1} bond in the infrared spectrum. Treatments for 10 minutes and one hour at room temperature gave little or no change when the spectra were obtained. Liquid chlorine under pressure can be used when it is considered desirable to speed up the reaction.

The chlorine treatment virtually eliminated the emission of residual dicyclopentadiene from a polymer strip as measured by gas chromatography. The measurement of residual DCPD involves the passage of a slow stream of gas over the strip of polymer. The monomer evolved is picked up by an absorbent in said gas. Every few minutes the gas is desorbed for passage into the gas chromatograph for measurement of the residual monomer.

The resistance of the chlorinated polymer was tested with a number of common reagents, as well as with toluene and 70% nitric acid. Toluene and nitric acid were chosen since neither the untreated polymer nor other polyolefins resist them. The chlorinated Polymers 1 and 2 resisted 37% hydrochloric acid, 80% sulfuric acid, 70% nitric acid, 5.25% sodium hypochlorite and acetone for three days at room temperature. The materials swelled 12-15% in ethyl acetate. The protection against 70% nitric acid was considerable (a 0.5-0.7% gain in weight versus a 26% loss in weight for the untreated polymer over a three day span).

EXAMPLE 2

In this Example the polymer was treated with aqueous chlorine. A 4 mm x 4 mm square cut from a 1/8 inch plaque of polymer 2 was placed in water. Chlorine gas from a cylinder was passed through for three hours. Chlorine flow was then turned off. The polymer was left in the aqueous medium overnight, for a total of 23 hours. The polymer was removed, then washed well with water and dried in an open dish, then in a dessicator. The infrared spectrum showed a hydroxyl band at 3565 cm^{-1}, no remaining double bond at 3048 cm^{-1}, CHCl at 1275 cm^{-1}, C-OH at 1087 cm^{-1} and CCl at 818-667 cm^{-1}. Hypochlorous acid added to the polymer's double bonds. This treatment reduces the rate of emission of residual monomer by 98%. There was no change evident in the size or shape of polymer strips containing EPDM or SBR rubber when treated with aqueous, chlorine for 10 days at 90 °C. The samples gained about 3% in weight.

EXAMPLE 3

In Example 3, strips of dicyclopentadiene polymer were fluorinated. Fluorine is such a reactive gas that normally it has to be diluted with an inert gas to control the reaction (to prevent charring), as in Set B below. However, with poly(DCPD), the dilution proved to be unnecessary.

The treated strips showed greatly increased resistance to toluene and 70% nitric acid. Fluorination also reduced the rate of loss of residual DCPD monomer by about 99%.

The fluorinated layer produced is thin, about 5 to 10 microns thick. Photoacoustic infrared spectroscopy penetrates 15 to 25 microns into the polymer. If this thickness had been fluorinated completely, all the bands attributable to double bonds and carbon-hydrogen bonds would have disappeared.

Sets of Polymer 1 strips (three strips of 7/8 inch by 3 inches per set) were fluorinated in a one inch diameter nickel tube. Six sets of conditions were used. Unless otherwise stated, all fluorinations were carried out at the summer ambient temperature of between about 31 and 34 °C. (A) The control material was not fluorinated. Other samples were subjected to the following treatments: (B) A second set of samples was treated initially with 1% fluorine for 2 hours, increased to 2% fluorine for 2 hours, then 4% fluorine for 2 hours, 8% fluorine for 2 hours, 16% fluorine for 4 hours, and finally 100% fluorine for 9 hours. (C) A third set of samples were treated with 10% fluorine for 4 hours, and then with 100% fluorine for 17 hours. (D) A fourth set of samples was treated with 10% fluorine for 4 hours, then with 100% fluorine for 17 hours, and then the temperature was raised to 50 °C for 4 hours. (E) A fifth set of samples was treated with 10% fluorine for 4 hours, then with 100% fluorine for 4 hours at 50 °C. and last with 100% fluorine for 4 hours at 70 °C. (F) A sixth and final set of samples was treated with 100% fluorine for 1.5 hours at 60 °C.

Photoacoustic infrared spectroscopy of the surface of some samples showed a reduction in the amount of double bonds at 3046, 1408 and 977 cm^{-1} and a reduction of CH bonds at 2932, 2895, 2855 and 1432 cm^{-1} . Strong CHF absorption was present at 1313, 1287, 1248, 1213 and 1183 cm^{-1}.

A strip of fluorinated polymer D immersed in toluene increased in weight 0.16% in 17 hours and 0.7% in 41 hours. A strip of fluorinated polymer F showed a 0.4% gain in weight in 24 hours. Untreated samples increased 82% by weight in only 18 hours.

A 19 mm portion of a sample was immersed halfway in 70% nitric acid (with the newly cut edge out of the liquid at the top). After three days it had lost 0.3% in weight. A parallel trial showed a weight gain of 1.3% in three days and a gain over the original weight of 0.85% in 7 days. A complete strip of polymer F completely immersed in 70% nitric acid gained 0.4% in weight in 4 days. Untreated polymer lost 24% of its weight when immersed in 70% nitric acid for three days.

EXAMPLE 4

In this example, the DCPD polymer was treated by immersion in liquid bromine. A 0.85 x 3.75 cm strip of polymer 2 was covered with liquid bromine in a test tube. After one minute, the bromine was poured off. The strip was allowed to dry in an open dish in the hood. The infrared spectrum showed loss of the double bond band at 3048 cm^{-1}, some carbonyl band present at 1720 cm^{-1} and strong absorption of CH-Br at 1305, 1251 and 1171 cm^{-1}. Energy dispersive x-ray analysis and infrared microspectrometry on 20 micron sections cut by a microtome showed reaction to a depth of 60 microns. The rate of emission of residual dicyclopentadiene was reduced by 89%. Further reduction of the rate of emission will be achieved by longer exposure to the liquid bromine. The polymer brominated for 30 minutes (0.5 x 2.5 inch strip) exhibited significantly improved resistance to 70% nitric acid with a 1% gain in weight in 71 hours compared to a 26% loss in weight in a control sample. After 4 days in 70% nitric acid a second sample brominated for 30 minutes (0.5 x 1 inch strip) had gained 0.1% in weight compared to a 15% loss in a control sample.

EXAMPLE 5

In this example hypobromous acid was added to the polymer by treatment with bromine water. A 0.85 x 3.75 cm strip cut from a 1/8 inch thick plaque of polymer 2 was left in a stirred saturated solution of bromine in water for 24 hours. After removal from the solution, the strip was washed well with water, then dried first in an open dish and then in a dessicator. The infrared spectrum showed hydroxyl at 3528 cm^{-1}, only a faint trace of double bond remaining at 3048 cm^{-1}, ketone carbonyl at 1724 cm^{-1}, CHBr at 1306, 1298, 1248 and 1174 cm^{-1} and C-OH at 1081 cm^{-1}. This reduced the rate of emission of residual monomer by 100%. Samples treated with bromine water were resistant to 70% nitric acid with a 3% weight gain after 3 days.

A variety of halogen reagents have been shown to react with the double bonds in polydicyclopentadiene. Disappearance of cis double bonds appears to be faster than trans double bonds. The depth of penetration of the reagent varies with the time for the reaction. Reaction of many or all of the surface double bonds was found with chlorine, bromine, fluorine, aqueous chloride, and aqueous bromine. These substances all drastically reduced the rate of loss of residual monomer with no measurable amounts detectable after treatment with chlorine and aqueous bromine and 89% reduction with bromine, 99% with fluorine and and 98% with aqueous chlorine.

The reacted surfaces also improved the resistance of the polymer to toluene and 70% nitric acid, two reagents chosen because DCPD polymers and other strained ring polyolefins are not resistant to them. Chlorination, bromination and fluorination, as well as treatment with aqueous chlorine and aqueous bromine improved the resistance to 70% nitric acid. Only fluorination gave resistance to toluene.

Claims

1. A method for treating the surface of a thermoset polymer article prepared by polymerization of a strained ring polycyclic cycloolefin monomer comprising halogenating the surface of the article with a halogen, a pseudohalogen compound, or an interhalogen compound.

2. A method for treating the surface of a polymer article as claimed in claim 1, further characterized in that the surface of the article is halogenated with fluorine, chlorine or bromine.

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Claims

1. A method for treating the surface of a thermoset polymer article prepared by polymerization of a strained ring polycyclic cycloolefin monomer comprising halogenating the surface of the article with a halogen, a pseudohalogen compound, or an interhalogen compound.

2. A method for treating the surface of a polymer article as claimed in claim 1, further characterized in that the surface of the article is halogenated with fluorine, chlorine or bromine.

3. A method for treating the surface of a polymer article as claimed in claim 1, further characterized in that the surface of the article is halogenated with ClSCN, ISCN, INCO, $(SCN)_2$, INO_3, or BrN_3.

4. A method for treating the surface of a polymer article as claimed in claim 1, further characterized in that the surface of the article is halogenated with ICl, IF, or BrF.

5. A method for treating the surface of a polymer article as claimed in any of the preceding claims, further characterized in that the surface of the article is halogenated by exposure to a gas, a liquid or an aqueous solution.

6. A method for treating surfaces of polymer articles as claimed in any of the preceding claims, further characterized in that the polymer article is molded from poly(dicyclopentadiene) or a copolymer of dicyclopentadiene and another strained ring cycloolefin.

Patentansprüche

1. Verfahren zur Oberflächenbehandlung eines Duroplastpolymer-Artikels, der durch Polymerisation eines polycyclischen Cycloolefinmonomers mit gespanntem Ring hergestellt wurde, umfassend die Halogenierung der Oberfläche des Artikels mit einem Halogen, einer Pseudohalogenverbindung oder einer Interhalogenverbindung.

2. Verfahren zur Oberflächenbehandlung eines Polymerartikels gemäß Anspruch 1, weiterhin dadurch gekennzeichnet, daß die Oberfläche des Artikels mit Fluor, Chlor oder Brom halogeniert wird.

3. Verfahren zur Oberflächenbehandlung eines Polymerartikels gemäß Anspruch 1, weiterhin dadurch gekennzeichnet, daß die Oberfläche des Artikels mit ClSCN, ISCN, INCO, $(SCN)_2$, INO_3 oder BrN_3 halogeniert wird.

4. Verfahren zur Oberflächenbehandlung eines Polymerartikels gemäß Anspruch 1, weiterhin dadurch gekennzeichnet, daß die Oberfläche des Artikels mit ICl, IF oder BrF halogeniert wird.

5. Verfahren zur Oberflächenbehandlung eines Polymerartikels gemäß einem der vorhergehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß die Oberfläche des Artikels halogeniert wird, indem sie einem Gas, einer Flüssigkeit oder einer wässrigen Lösung ausgesetzt wird.

6. Verfahren zur Oberflächenbehandlung eines Polymerartikels gemäß einem der vorhergehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß der Polymerartikel aus Poly(dicyclopentadien) oder einem Mischpolymer aus Dicyclopentadien und einem anderen Cycloolefin mit gespanntem Ring geformt wird.

Revendications

1. Procédé pour traiter la surface d'un article en polymère thermodurci, préparé par la polymérisation d'un monomère du type cyclooléfine polycyclique annulaire soumise à contrainte, comprenant l'halogénation de la surface de l'article avec un halogène, un composé du type pseudohalogène ou un composé du type interhalogène.

2. Procédé pour traiter la surface d'un article en polymère suivant la revendication 1, caractérisé en ce que la surface de l'article est halogénée avec du fluor, du chlore ou du brome.

3. Procédé pour traiter la surface d'un article en polymère suivant la revendication 1, caractérisé en ce que la surface de l'article est halogénée avec C1SCN, ISCN, INCO, $(SCN)_2$, INO_3 ou BrN_3.

4. Procédé pour traiter la surface d'un article en polymère suivant la revendication 1, caractérisé en ce que la surface est halogénée avec ICl, IF ou BrF.

5. Procédé pour traiter la surface d'un article en polymère suivant l'une quelconque des revendications précédentes, caractérisé en ce que la surface de l'article est halogénée par exposition à un gaz, un

liquide, ou une solution aqueuse.

6. Procédé pour traiter des surfaces d'articles en polymère suivant l'une quelconque des revendications précédentes, caractérisé en ce que l'on moule l'article en polymère à partir de poly(dicyclopentadiène) ou d'un copolymère du dicyclopentadiène et d'une autre oléfine cyclique soumise à contrainte.