Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 687−695

polymer

www.elsevier.com/locate/polymer

Polysiloxane−poly(fluorinated acrylate) interpenetrating polymer networks: Synthesis and characterization

Vincent Darras [a], Odile Fichet [a], Françoise Perrot [a], Sylvie Boileau [b], Dominique Teyssié [a,*]

[a] Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI), Université de Cergy-Pontoise − 5, mail Gay-Lussac, Neuville-sur-Oise, 95031 Cergy-Pontoise Cedex, France
[b] Laboratoire de Recherche sur les Polymères, UMR 7581 CNRS, 2, rue H. Dunant, 94320 Thiais, France

Received 21 July 2006; received in revised form 27 November 2006; accepted 28 November 2006

Abstract

Combinations of fluorinated and silicone based elastomers were elaborated through the *in situ* synthesis of interpenetrating polymer networks (IPNs). The PDMS network was formed by dibutyltindilaurate catalyzed addition between the hydroxy end groups of α,ω-(3-hydroxypropyl)-polydimethylsiloxane (PDMS) and a pluriisocyanate cross-linker. The poly(fluorinated acrylate) (polyAcRf6) network was obtained from free-radical copolymerization of a fluorinated acrylate with ethylene glycol dimethacrylate in the presence of dicyclohexyl peroxydicarbonate as the initiator. IPNs with different relative weight proportions of the fluorinated vs silicone partners were characterized by DMTA and DSC. Density refractive index and contact angle measurements reveal a satisfactory interpenetration degree of PDMS and polyAcRf6 networks. In addition, these materials present an unusual variation of density values and of the surface properties as a function of the relative weight composition.

Keywords: Polydimethylsiloxane; Fluorinated acrylate; Interpenetrating polymer network

1. Introduction

Various strategies have been developed in order to design fluorine-containing elastomers maintaining rubber-like elasticity in extremely severe environments including exposure to high temperatures and corrosive chemicals. The synthesis of fluorinated compounds leading to elastomers showing high solvent resistance, thermal stability, low-temperature flexibility and high fluorine content presents some internal conflicts because of the repulsions between the hydrocarbon and fluorocarbon groups which are necessarily associated in the same molecule. In addition, these compounds generally are liquid or waxy solids above 0 °C. In order to prevent permanent flow deformation under an imposed strain, these flexible macromolecules must be cross-linked.

Fluorinated polysiloxane single networks have been prepared by sol−gel reaction of fluorinated polysiloxanes bearing terminal trialkoxysilane moieties with silanol cross-linkers [1], or fluorinated polysiloxanes bearing silanol end groups with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-triethoxysilane [2]. Similar single networks were also synthesized by hydrosilylation reaction of tetravinyltetramethylcyclotetrasiloxane (D_4^{Vi}) [3], divinyltetramethyldisiloxane [4] or fluorinated divinyl telechelic polysiloxane [5] with polysiloxanes containing fluorinated side chains and Si−H groups. For example, Fuduka et al. [6] have synthesized networks starting from perfluorinated vinyl ether end chains which react on Si−H terminated polysiloxanes bearing $-CH_2-CH_2-C_8F_{17}$ side-groups. Those fluorinated polysiloxane networks are mainly used as protecting coatings. However, the synthesis pathways leading to the telechelic precursors of those networks do not allow a fine tuning of the molar mass and polymolecularity, as well as of their functionality which should be as close as possible to two. In addition, fluorinated polysiloxane networks do not show convenient

---

* Corresponding author. Tel.: +33 1 34 25 70 50; fax: +33 1 34 25 70 70.
E-mail address: dominique.teyssie@chim.u-cergy.fr (D. Teyssié).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.11.058

mechanical properties at room temperature which restrains the development of these materials in new applications.

An adequate solution, which could lead to the elaboration of materials endowed with the desirable characteristics of fluorinated polysiloxane networks without showing their drawbacks, is to combine two independent polymers showing polysiloxane properties on one hand, and fluorinated ones on the other hand, into an interpenetrating polymer network (IPN) architecture. The aim of the elaboration of such types of polymer associations in general is to obtain materials with better mechanical properties, an increased resistance to degradation and a potential synergy of the properties of their components.

IPNs are defined as combinations of two or more polymer networks synthesized in juxtaposition [7,8]. The entanglement of two cross-linked polymers leads to forced miscibility compared with usual incompatible blends, and the resulting materials exhibit a good dimensional stability. IPNs can be prepared through an *in situ* synthesis where all reactants are mixed together. According to this strategy, the syntheses of the two networks are started at the same time leading either to their simultaneous or sequential formation. Hence, the reaction mechanisms leading to the formation of the two network partners must be of different nature, otherwise a single copolymer network (bicomponent network or co-network) is formed through crossed reactions.

In the present work, the synthetic pathway for preparing IPNs composed of polydimethylsiloxane (PDMS) and a poly(fluorinated acrylate) (polyAcRf6) is described. The synthesis involves an *in situ* process where the two networks are then formed more or less simultaneously as it will be shown. The conversions as a function of time of the reactive functions involved in the synthesis of each network during the IPN formation have been investigated by near FTIR spectroscopy. In order to examine the extent of network interpenetration, thermomechanical properties, density and refractive index of the resulting materials have been studied as a function of PDMS/polyAcRf6 composition. Finally the surface properties of those IPNs have been characterized by contact angle measurements.

2. Experimental section

2.1. Materials

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol (Aldrich), dibutyltindilaurate (DBTDL, Aldrich), ethylene glycol dimethacrylate (EGDMA, Aldrich), acryloyl chloride (Acros) and Desmodur® N3300 (Bayer) (NCO content: 21.8 ± 0.3 wt% according to the supplier) are used as received. This last compound is described as an isocyanurate mixture resulting from the condensation of three to several hexamethylene diisocyanate molecules and mainly composed of mono-, di- and tri-isocyanurates with a global functionality higher than 2 [9]. Thus mere "tris(6-isocyanatohexyl)isocyanurate" is not a proper description and the compound is referred to as the cross-linking agent. Dicyclohexylperoxydicarbonate (DCPD, Groupe Arnaud) is dried under vacuum before use. Toluene (Carlo Erba, puro) and dichloromethane (CH_2Cl_2, Carlo Erba) are distilled and dried before use. 1,1,2-Trichloro-2,2,1-trifluoroethane (F113) and α,ω-(3-hydroxypropyl)poly(dimethylsiloxane) (PDMS oligomer) are kindly provided by Atochem and Rhodia, respectively. PDMS oligomer ($Mn_{SEC} = 1140$ g mol^{-1}, Ip = 2 in THF, $Mn_{NMR} = 1100$ g mol^{-1} in $CDCl_3$) is dried under vacuum before use.

2.2. Material synthesis

α,ω-(3-Hydroxypropyl)poly(dimethylsiloxane) (1 g, 1.75×10^{-3} OH mol) and Desmodur® N3300 (0.40 g, 2.11×10^{-3} NCO mol, [NCO]/[OH] = 1.2) are dissolved in 2 mL toluene to which the catalyst DBTDL (16 mg, 2.53×10^{-5} mol, [DBTDL]/[OH] = 0.014) is added. The mixture is poured under argon into a mould made from two glass plates clamped together and sealed with a 1 mm thick Teflon® gasket. The mould is heated in an oven at 55 °C for 15 h. After release from the mould, a transparent film is obtained after taking off toluene under vacuum.

The fluorinated acrylate (AcRf6) is synthesized as follows: 7.28 g of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (0.02 mol), 2.43 g triethylamine (0.024 mol) and 100 mL CH_2Cl_2 are placed in a three-neck flask fitted with a condenser. Acryloyl chloride (1.79 mL, 0.022 mol) is added dropwise at 0 °C. Then, the mixture is stirred at 40 °C for 6 h. At the end of the reaction, the mixture is washed several times with a sodium hydroxide solution to neutral pH. The crude product is dried on $MgSO_4$. After filtration, the solvent is eliminated under vacuum. The obtained product, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate (PolyAcRf6) is purified on a silica column with CH_2Cl_2 as the eluent and characterized by ^{1}H NMR ($CDCl_3$).

A single fluorinated network is prepared as follows: AcRf6 (1 g, 2.4×10^{-3} mol), EGDMA (24 mg, 1.2×10^{-4} mol, [EGDMA]/[AcRf6] = 0.05) and DCPD (3.8 mg, 1.3×10^{-4} mol, [DCPD]/[C=C] = 0.05) are mixed under argon for 30 min. The mixture is poured into a mould made from two glass plates clamped together and sealed with a 1 mm thick Teflon® gasket. The mould is heated in an oven at 55 °C for 15 h and a transparent film is obtained. The synthesis of this single network does not require a solvent.

A PDMS/polyAcRf6 (50/50) IPN is synthesized as follows (Scheme 1): α,ω-(3-hydroxypropyl)poly(dimethylsiloxane) (PDMS oligomer, 1 g, 1.75×10^{-3} OH mol) is dissolved in 2 mL toluene under argon together with 0.40 g Desmodur® N3300 (2.11×10^{-3} NCO mol, [NCO]/[OH] = 1.2), 1 g AcRf6 (2.4×10^{-3} mol), 24 mg EGDMA (1.2×10^{-4} mol, [EGDMA]/[AcRf6] = 0.05) and 3.8 mg DCPD (1.3×10^{-4} mol, [DCPD]/[C=C] = 0.05). Then, 16 mg DBTDL (2.53×10^{-5} mol, [DBTDL]/[OH] = 0.014) is added just before introducing the mixture into a mould as described previously. The mould is heated in an oven at 55 °C for 15 h and toluene is then taken off under vacuum.

IPNs with polyAcRf6 contents ranging from 25 to 75% by weight are synthesized keeping the same proportions among monomer, cross-linker and catalyst or initiator as described for the synthesis of each single network. All investigated