



# Toughening diene elastomers by strong hydrogen bond interactions



Ming-Chao Luo, Jian Zeng, Xuan Fu, Guangsu Huang\*, Jinrong Wu\*\*

State Key Laboratory of Polymer Material Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu, 610065, PR China

## ARTICLE INFO

### Article history:

Received 26 July 2016

Received in revised form

6 October 2016

Accepted 27 October 2016

Available online 28 October 2016

### Keywords:

Toughness

Diene elastomers

Hydrogen bonds

## ABSTRACT

Introducing reversible hydrogen bonds as sacrificial bonds is an emerging strategy to improve the toughness of elastomers. However, binary hydrogen bonds are not strong enough and highly dynamic, and thus have only a moderate toughening effect. Here we demonstrate that quadruple hydrogen bonds have a remarkable toughening effect for diene elastomers. To fabricate the quadruple hydrogen bonds toughened elastomer, we graft 2-ureido-4[1H]-pyrimidinone (UPy) groups onto the backbone of polyisoprene (PI). The UPy groups dimerize to form strong hydrogen bonds which have higher bond energy than binary hydrogen bonds. Compared with weak hydrogen bonds with the same mole fraction, the strong hydrogen bonds lead to higher reversible crosslinking density and slower chain mobility of the elastomer; this enables higher energy dissipation as the elastomer is subjected to deformation. As a result, the introduction of UPy significantly increases both the toughness and the tensile strength of the elastomer. Moreover, unlike covalent sacrificial bonds, the hydrogen bonds of UPy are dynamic and show the re-association of sacrificial bonds at room temperature, as evidenced by recovery of hysteresis loop during cyclic tensile tests. This work will not only greatly extend our understanding on the different toughening effects of weak and strong hydrogen bonds, but also help us to rationally design tougher elastomers.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Diene elastomers, such as natural rubber (NR), polyisoprene (PI), and polybutadiene (PB), are widely used in tires, seals, dampers, gloves and shoes. These applications require elastomers with high toughness and fracture energy. However, the critical fracture energy of unfilled elastomers is only about 50 J/m<sup>2</sup>, according to the calculation of Lake-Thomas theory [1]. To improve the toughness of elastomers, the most common strategy is to incorporate nanofillers. The addition of nanofillers introduces significant energy dissipation through the break of filler network, yielding of bound rubber on the filler surfaces and friction between filler and rubber molecules [2,3]. This high level of energy dissipation greatly improves the toughness of elastomers. Nevertheless, special surface modification and processing technology are needed to disperse nanofillers [4–8]. Moreover, the processing of nanofillers usually causes health and environmental issues. These drawbacks strongly motivate us to exploit new strategies of toughening elastomers.

Recently, an elegant progress in toughening elastomers is achieved by introducing sacrificial bonds. The sacrificial bonds can dissipate energy and redistribute stress before the failure of elastomers, leading to improved toughness of elastomers [9–12]. Inspired by this concept and the work of double network hydrogels [13–15], Creton and co-workers [9] synthesized double/triple network elastomers, in which the first network chains are pre-stretched. The pre-stretched chains easily break upon deformation, and thus serve as sacrificial bonds and dissipate energy. As a result, the fracture energy of the double/triple network elastomers is as high as 5000 J/m<sup>2</sup>. Nevertheless, the sacrificial bonds in these elastomers are irreversible covalent bonds, which once break never reform. Circumventing this limitation requires us to replace the irreversible sacrificial bonds with reversible ones. Hydrogen bonds can be ideal reversible sacrificial bonds, as they easily break and reform due to their lower bond energy than covalent bonds and their dynamic nature [16–20]. Hovelmann and co-workers [21] grafted urazole groups onto covalently crosslinked PB networks. The urazole groups form binary hydrogen bonds, which serve as sacrificial bonds. However, the tensile strength and strain at break of the modified PB elastomer are only 0.6–1.6 MPa and 40%–60%, respectively. Other works also suggest that binary hydrogen bonds have a moderate toughening effect for elastomers, due to their low

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [guangsu-huang@hotmail.com](mailto:guangsu-huang@hotmail.com) (G. Huang), [wujinrong@scu.edu.cn](mailto:wujinrong@scu.edu.cn) (J. Wu).

bond energy [22,23]. Quadruple hydrogen bonds, such as the dimerization of 2-ureido-4[1H]-pyrimidinone (UPy) groups, have higher bond energy [24,25], which means more energy is needed to break these strong hydrogen bonds. Thus, we can envision that introducing strong hydrogen bonds may increase energy dissipation and toughness of elastomers.

Here, we introduce UPy motifs into covalently crosslinked PI elastomers. The UPy motifs dimerize to form strong hydrogen bonds, which serve as reversible sacrificial bonds. To demonstrate the superiority of strong hydrogen bonds, we also introduce hydroxyl groups into covalently crosslinked PI elastomers as a control. We find that the strong hydrogen bonds lead to higher effective crosslinking density and slower molecular dynamics of the elastomer network, thus enabling higher energy dissipation than weak hydrogen bonds. As a result, the UPy groups toughened elastomers have both higher toughness and mechanical strength compared with the hydroxyl groups toughened elastomers. This work on the different toughening effects of weak and strong hydrogen bonds will not only greatly extend our understanding on toughening elastomers using reversible sacrificial bonds, but also help us to rationally design tougher elastomers.

## 2. Experimental section

### 2.1. Materials

PI (GPC data:  $M_n = 241468$  g/mol,  $DPI = 3.893$ ) was purchased from Shanghai Sanlian Co., Ltd. 3-Chloroperoxybenzoic acid (MCPBA, 85%), 2-amino-4-hydroxy-6-methylpyrimidine (98%), hexyl diisocyanate (98%), and dibutyltindilaurate (95%) were purchased from Adamas Reagent Co., Ltd. Tetrahydrofuran (THF) was purchased from Shanghai Titan Scientific Co., Ltd and used without further purification. Hydrochloric acid (HCl, 36%) and chloroform were purchased from Sichuan Xilong chemical Co., Ltd. Curing reagents including sulfur, zinc oxide (ZnO), *N*-cyclohexyl-2-benzothiazolesulfenamide (CZ) and stearic acid (SA) were provided by Sichuan Haida Rubber Group Co., Ltd.

### 2.2. Preparation of PI with hydroxyl groups (HPI)

20.4 g of PI (0.3 mol isoprene units) was first dissolved in 450 mL of THF in a 1 L one-neck round-bottom flask equipped with magnetic stirrer. A solution of MCPBA in 50 mL THF was first prepared and then transferred into a 100 mL dropping funnel. It was added dropwise at room temperature into the PI solution. To prepare epoxidized PI (EPI), the reaction mixture was then further stirred for another 5 h. After 6 h, a solution of HCl in 50 mL THF was added dropwise at room temperature to the EPI solution and the reaction mixture was stirred for 4 h. Then the solution was added to methanol for precipitation. The product (HPI) was dried at 50 °C under vacuum for 2 days.

### 2.3. Preparation of PI with UPy groups (UPI)

According to the previous method [26], the UPy groups linked to a reactive isocyanate group (2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]-pyrimidinone, UPy-NCO) were prepared. To a solution of hydrochlorinated PI in 700 mL chloroform, UPy-NCO was added. After addition of 2 drops of dibutyltindilaurate, the resulting solution was stirred at 60 °C for 16 h. After the chloroform was removed, the resulting material was dried at 50 °C under vacuum for 2 days.

### 2.4. Preparation of covalently crosslinked elastomers (PI-OH and PI-UPy)

To chemically crosslink HPI and UPI, they were masticated on a two-roll mill with 1 mm roller spacing and blended with SA, ZnO, CZ, and sulfur. The formula of the curing reagents is as follows: elastomers 100 phr, SA 2 phr, ZnO 5 phr, CZ 1 phr, and sulfur 2 phr. PI-OH and PI-UPy with a thickness of 1 mm were obtained by compression curing in a hydraulic press at 143 °C for 18 min. PI-OH-*x* and PI-UPy-*x* are used to represent the PI-OH and PI-UPy with *x*% mole fraction of hydroxyl and UPy groups, respectively. The synthetic details and process are shown in Table 1 and Scheme 1, respectively.

### 2.5. Characterization

#### 2.5.1. Fourier transform infrared (FTIR)

The FTIR spectra were measured at room temperature using Thermo Scientific Nicolet iS50 FTIR with a resolution of 4  $\text{cm}^{-1}$ . Attenuated total reflection with SeZn crystal was used to obtain the FTIR spectra. The wavenumber range was from 4000  $\text{cm}^{-1}$  to 650  $\text{cm}^{-1}$ .

#### 2.5.2. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were measured in a tensile mode on a Q800 DMA (TA Instruments) under a nitrogen atmosphere. The dimensions of the specimens tested were 12 mm  $\times$  6.5 mm  $\times$  1 mm. The DMA spectra were performed at heating rate of 3 °C/min and a frequency of 1 Hz. The temperature range was –100 °C to 100 °C. In all cases a preload force of 0.01 N was applied.

#### 2.5.3. Broadband dielectric spectrum (BDS)

Dielectric measurements were performed over a frequency range of  $10^{-1}$ – $10^7$  Hz on a Novocontrol Concept 50 system with Alpha impedance analyzer and Quatro Cryosystem temperature control. The disk-shaped film of about 1 mm thickness was placed between two parallel electrodes with 20 mm diameter. BDS spectra were collected in a temperature range from –70 °C to 50 °C with 10 °C intervals.

The analyses of the dielectric spectra are made by using Havriliak and Negami (HN) empirical equation. In this model, the frequency dependences of the dielectric complex ( $\epsilon^*$ ) can be described by

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau_{HN})^\alpha]^\beta} \quad (1)$$

where  $\Delta\epsilon = \epsilon_s - \epsilon_\infty$  is the dielectric strength,  $\epsilon_s$  and  $\epsilon_\infty$  are the relaxed and unrelaxed values of dielectric constant, the parameters  $\alpha$  and  $\beta$  ( $0 < \alpha, \alpha\beta \leq 1$ ) define the symmetrical and asymmetrical broadening of the loss peak, and  $\tau_{HN}$  is the characteristic relaxation time.

The relation between  $\tau_{HN}$  and  $\tau_\alpha$  is given by

**Table 1**  
The formula for PI-OH-4 and PI-UPy.

Sample	Degree of modification (mol %, based on isoprene units)	MCPBA (g)	HCl (g)	UPy-NCO (g)
PI-OH-4	0	2.44	2.44	0
PI-UPy-1	1	2.44	2.44	0.88
PI-UPy-2	2	2.44	2.44	1.76
PI-UPy-3	3	2.44	2.44	2.64
PI-UPy-4	4	2.44	2.44	3.52

Download English Version:

<https://daneshyari.com/en/article/5178646>

Download Persian Version:

<https://daneshyari.com/article/5178646>

[Daneshyari.com](https://daneshyari.com)