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Smart polyolefins feeling the force: Color changeable poly(ethylene-vinyl acetate) and poly(ethylene-octene) in response to mechanical force

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ABSTRACT

Spiropyran (SP) mechanophore cross-linker was covalently incorporated into two widely used polyolefins, poly(ethylene-vinyl acetate) (EVA) and poly(ethylene-octene) (EOC), through facile cross-linking by peroxide under hot press. It was found that (1'-(2-(methacryloyloxy)ethyl)-3′,3′ dimethylspiro [chromene-2,2'-indolin]-6-yl)methyl methacrylate (SP3) could not be thermally driven to merocyanine (MC) in polyolefins during high temperature cross-linking, which is superior to other types of SP mechanophores used for polymer processing. The force-induced ring-opening reaction of SP-to-MC was demonstrated on SP3-cross-linked EVA. It was found that increasing the SP content resulted in earlier activation and that more MC was driven from SP at a slower strain rate. When held at constant strain, MC gradually reverted to SP. The mechanoactivation of SP was also investigated for SP3-cross-linked EOC. This work represents the first example of color-changeable polyolefins in response to mechanical force and demonstrates the feasibility of applying mechanophores to widely-used commercial polyolefins for stress sensing.

1. Introduction

Over the past few years, there has been an increasing interest in mechanoresponsive smart materials, which can transfer mechanical stimuli into other forms of energy [1–3]. To prevent the catastrophic damage or failure of materials, it is crucial to monitor stress fraction, fatigue, and hysteresis. The most prevalent method to design and develop force sensitive material is to incorporate a mechanoresponsive motif ("mechanophore"), containing a labile bond that is subject to change under mechanical force. Among all the mechanochemistry, some allow for direct visual warnings through color changing, fluorescence emission and light-emitting [4–6].

Regarding color-changeable materials in response to mechanical force, employing colorimetric mechanophore spiropyran (SP) in polymer was pioneered by Sottos, Moore, and their co-workers [4,5,7–12]. SP, covalently incorporated into a polymer, undergoes electrocyclic-ring-opening reaction when subjected to stress and yields a purple/blue colored fluorescent merocyanine (MC) form. Bis(adamantly)-1,2-dioxetane was reported to have the feature of mechanoluminescence by Sijbesma, Meijer, and their co-workers [6,13]. These mechanophores allow for stress visualization with high spatial and temporal features, facilitating the prevention of catastrophic failure.

Prior work has demonstrated incorporating SP mechanophores into poly(methyl acrylate) [4,5,10,14], poly(methyl methacrylate) [4,8,9,12,14], poly(urethane) [11,15], poly(dimethylsiloxane) [16–18], poly(ε-caprolactone) [19], and carefully designed elastomers such as polystyrene-b-poly(*n*-butylacrylalte)-SP-poly(*n*-butylacrylalte)-b-polystyrene [20,21]. Recently, Meng et al. introduced SP mechanophore into CO_2-breathing microgels [22]. However, incorporation of mechanophores into polyolefins for stress/strain sensing has not been reported. Polyolefins are most commonly and widely used and account for over half of the total polymers consumed around the world. In past decades, we have witnessed the ever-expanding application of polyolefins in our daily life, such as medical, packaging, sports, cable, wire coatings and so on. Rendering the most widely used polyolefins with mechanical force

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sensitivity has many potential applications, and thus deserves to be investigated. Therefore, we propose to incorporate SP mechanophore into polyolefins to demonstrate the idea.

To test the idea, we chose poly(ethylene-vinyl acetate) (EVA) as a platform because of its excellent flexibility, resilience, toughness and crack resistance [23]. Also, its relatively high polarity is speculated to render high compatibility with SP mechanophore. A nonpolar polyolefin, poly(ethylene-octene) (EOC) was also selected as another candidate for SP mechanophore incorporation due to its excellent elasticity, good tear resistance, and long shelf life [24]. In this work, the preparation of mechanoresponsive polyolefins was achieved by cross-linking EVA or EOC using peroxide, during which SP mechanophore cross-linker was added as co-cross-linker. Fig. 1 illustrates the network of cross-linked EVA and EOC, consisting of two types of cross-links. One type of cross-links is formed by the termination of macroradicals (tertiary carbon and/or secondary carbon), and the other type is formed by free radical addition reaction and/or copolymerization of dimethyacrylate-containing SP cross-linker [23,25,26]. Covalently cross-linked into the polymer network, SP co-cross-linker indicates stress/strain by giving off purple/blue color during the deformation of polyolefins.

So far, there have been three types of SP mechanophore cross-linkers, including 1′,3′,3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]-5′,8-diyl bis(2-methylacrylate) (SP1) [4], (1'-(2-(methacryloyloxy)ethyl)-3′,3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-8-yl)methyl methacrylate (SP2), and SP3 [27], shown in Fig. 2. Both SP1 and SP2 are sensitive to UV irradiation and mechanical force, while SP3 is sensitive to mechanical force but not to UV due to the lack of the electron-withdrawing nitro group [27,28]. In this work, SP3-containing polyolefins were systematically investigated because unlike its counterpart no thermally driven SP-to-MC conversion was observed for SP3 under high temperature curing. The mechanical activation of SP3 under the uniaxial tensile test of EVA was studied. The effects of SP3 content, strain rate and stress relaxation on the mechanical activation of SP3 in EVA were investigated in detail. Mechanical activation of SP3-cross-linked EOC was also discussed. To the best of our knowledge, it is the first time that mechanophore is incorporated into polyolefins for stress/strain indication, which is of great importance for broadening the application of mechanochemistry and gaining insight into the force distribution in engineering polymers upon straining.

2. Experimental methods

2.1. Chemicals

EVA (25 wt% vinyl acetate content; melt index, 19 g/10 min under the load of 2.16 kg; density, 0.941 g/cm^3) and dicumyl peroxide (DCP, 98%) were purchased from Aldrich. EOC (melt index, 0.5 g/10 min under the load of 2.16 kg; density, 0.863 g/cm^3) was purchased from Dow. All the chemicals were used as received unless stated otherwise. SP3 and SP2 were synthesized via the methods described by Meng et al. [27].

2.2. Sample preparation

Five samples of cross-linked EVA containing various SP3 contents were prepared using a hot press. DCP was used as initiator and SP mechanophore was added as co-cross-linker. The SP contents in the five runs were 0 mg, 8 mg, 16 mg, 32 mg and 48 mg,

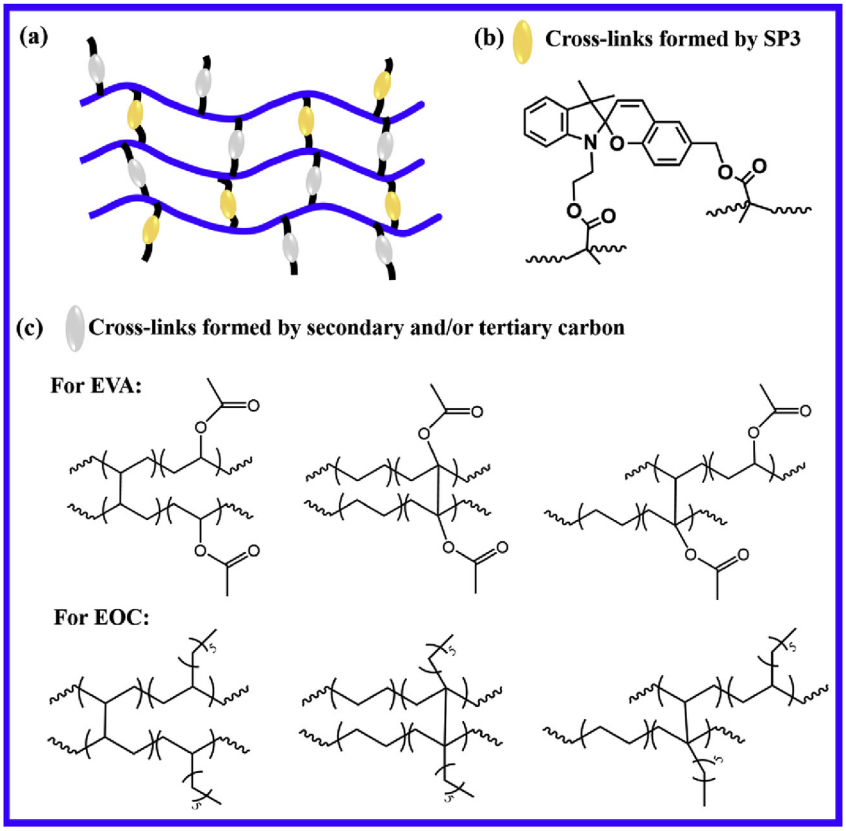

Fig. 1. (a) EVA and EOC polymer network containing both SP cross-links and cross-links from secondary and/or tertiary carbon of EVA and EOC; (b) Chemical structure of the SP3 cross-links; (c) Chemical structure of the cross-links formed by secondary and/or tertiary carbon of EVA and EOC.