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Self-assembled elastomer nanocomposites utilizing C_{60} and poly(styrene-b-butadiene-b-styrene) via thermally reversible Diels-Alder reaction with self-healing and remolding abilities

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In this article, C_{60} could be co-assembled into PB phase of the furan modified poly(styrene-b-butadiene-b-styrene) (SBS) via Diels-Alder (DA) reaction at the molecular level. The morphology of SBS could be effectively tailored by the incorporation of C_{60} and even small amount of C_{60} could lead to great change in the morphologies of SBS. Three types of morphologies of SBS could be observed as the content of C_{60} was increased from 0.1 to 2 wt%, which included honeycomb like, worm-like bi-continuous phase and their intermediate transition state. In the meantime, it was unexpectedly found that C_{60} could be used as effective crosslinking agents to build the network toward the furan modified SBS via DA reaction. Therefore, its solvent resistance, elastic resilience and tensile strength were greatly improved for the chemical crosslinking. Besides, due to the thermal reversible character for DA reaction, the hybrids based on SBS and C_{60} possessed the self-healing and remolding abilities via retro-Diels-Alder (rDA) reaction. All in all, C_{60} could provide the multiple functions toward the modification of SBS via DA reaction.

1. Introduction

C_{60} is the most prominent representative of the fullerene family [1]. As one of important carbon based nanomaterials (Fullerene, carbon nanotubes and graphene), C_{60} has clear structure and smallest unit similar with chemical compound compared with others. Considering the special aromatic character, the molecule shows quite high chemical reactivity [2,3]. Therefore, various fullerene derivatives have been synthesized based on its chemical reactivity. For example, addition of azomethine ylides to C_{60} was based on the 1,3-dipolar cycloaddition; the reaction between *N*-methylglycine (sarcosine), formaldehyde, and C_{60} led to the *N*-methylpyrrolidine derivative [4,5] and photochemical treatment of triethylamine with C_{60} has also led to fulleropyrrolidines [6]. Meanwhile, electron donor-acceptor interactions of fullerenes with triethylamine (TEA) resulted in fullerene-TEA covalent products [7] and so on. Among them, Diels-Alder reaction was one of the effective reactions for preparing the fullerene derivatives [8]. For the electron-withdrawing nature of C_{60}, it was an ideal dienophile for the Diels-Alder reaction. As reported, C_{60} could undergo the [4 + 2] DA cycloaddition with many reactive dienes including anthracene, tetracene, furan and cyclopentadiene and so on [9–15]. Recently, we have successfully prepared poly(styrene-b-butadiene-b-styrene) modified with furan groups (SBS-Fu) [16] via thiol-ene reaction and this type of modified elastomer could be used as an active “macromolecular diene” to take part in Diels-Alder (DA) reaction [17]. Therefore, C_{60} could react with this type macromolecular diene to construct C_{60} and elastomer hybrid based on Diels-Alder reaction via solution casting method.

In fact, it has been reported that fullerene derivative can be incorporated into the polymer matrix to build different morphology for polymer, which finally result in different properties. For example, Nguyen' group has reported the change in morphology of the poly(3-hexylthiophene)(P3HT)–fullerene derivative triblock copolymer in the process of self-assembly based on the charge-transport interaction [18]. In their system, the morphology of P3HT for the hole and electron transporting networks can be controlled and adjusted simultaneously with the presence of fullerene derivative. For our system, SBS elastomer is a kind of three block copolymers composed of PS hard and PB soft

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block. The PS and PB block could be self-assembled to establish the phase separation structure where PS hard block could be used as physical crosslinking sites for PB phase [19,20]. In the earlier research work, people usually find that C_{60} has strong physical interaction with PS block via л-л conjugation [21]. However, in our system, C_{60} could be also co-assemblied into the SBS on the molecular level via DA reaction with furan groups on the PB block. Therefore, different kinds of morphologies would be obtained for SBS based on these two interaction modes. In the meantime, we had to resolve two interesting problems; one problem was how did the properties of SBS change via this chemical assembly and these properties include the size stability, solvent resistance, and mechanical properties? The other problem was what kind of interaction (physical or chemical interaction) was more effective on affecting the final morphologies and properties. Answers for these questions would provide very important information to establish the relationship between the self-assembly morphologies and final properties for the copolymers.

In addition, this hybrid system could also be provided as a new model for the recycling of the polymer based hybrids. In fact, SBS was a typical representative of thermoplastic elastomer [22]. They have rubber like properties at room temperature and could be thermal remolding like the plastic materials at high temperature. SBS has been widely used in various areas, such as adhesives, impact modifiers and toughening agent in engineering plastics [23–28]. However, several drawbacks including poor solvent resistance and elastic resilience associated with physical cross-links limit its application. People have designed several methods to improve these two properties. For example, our group [29] has applied the benzoxazine group into PB phase via thiol-ene click reaction, both solvent resistance and elastic resilience has improved greatly via two steps of crosslinking reaction. However, the thermal remolding ability was lost, which was a very important character for thermoplastic elastomer. Therefore, improving the solvent resistance and elastic resilience without sacrificing its thermal remolding ability is till great challenge towards modification of SBS. In our research work, this kind of hybrid based on C_{60} and SBS-Fu via DA reaction could provide a balanced solution to these problem due to several following reasons: first, C_{60} could react with furan groups branched to PB block via DA reaction in the molecular level and this kind of interaction via self-assembly of PB phase, PS phase and C_{60} on the smallest size scale could improve its poor solvent resistance and elastic properties effectively. Second, the thermal reversible character for Diels-Alder reaction could still render this type of hybrid with good thermal remolding and high efficient self-healing properties [30–39]. Most of important, unlike other carbon based nanomaterials such as carbon nanotubes and graphene, this kind of hybrid based on C_{60} and the furan modified SBS copolymer could provide powerful model to investigate the interaction between polymer chains and inorganic fillers due to their interaction at molecular level. In this way, the relationship between structure variation and mechanical properties could be clearly established via tailoring the content of C_{60} and the related research work based on this novel type of hybrid has never been reported elsewhere as far as we know.

In this paper, we focused on the hybrids basing on co-assembly of C_{60} and SBS-Fu at the molecular level for both chemical and physical interactions. Due to their chemical reaction via Diels-Alder, C_{60} could even act as effective crosslinking agents toward furan modified SBS to improve the mechanical properties greatly and the assembly morphologies for SBS could be changed considerably with the presence of C_{60}. In the meantime, the crosslinking network could also be broken to liberate the chains via the rDA reaction to give the hybrids with abilities of self-healing and remolding. These two important natures could be combined together to design the final properties via different morphologies by assembly between C_{60} and copolymers and ensure this novel hybrids to possess good recycling ability.

2. Experiment part

2.1. Materials

Toluene was purchased from Sinopharm Chemical Reagent Co., Ltd. Poly(styrene-b-butadiene-b-styrene) (70% PB block contained, Mw~ 153000–185000) and C_{60} were purchased from Sigma-Aldrich. Furfuryl mercaptan was purchased from J&K Scientific Ltd. All the reagents were used as received.

2.2. The modification of SBS with furfuryl mercaptan(SBS-20Fu)

The furan modified SBS was obtained as reported in our previous work [16]. SBS (70% PB block contained, Mw~153000–185000, linear polymer), furfuryl mercaptan and the photoinitiator I907 were dissolved in toluene. The content of furfuryl mercaptan was calculated based on the double bonds content of PB block in SBS. In this article, grafting ratio of the furan groups was fixed at 20% of the double bonds on SBS chains and the modified SBS was named as SBS-20Fu. The addition of furfuryl mercaptan was 20% of the molar of the double bond on PB block of SBS. Its recipe was as follows: 1 g SBS and 0.296 g furfuryl mercaptan were dissolved in 10 ml toluene with trace amounts of photoinitiator I907. Then the solution was stirred at room temperature under irradiation with 365 nm UV light for 12 h. The branching ratio of furan groups has been proved be almost the same as the addition content of furfuryl mercaptan due to the high efficiency of thiol–ene click reaction with ^{1}HNMR, FTIR and elemental analysis in our previous work. The ^{1}H NMR and FTIR spectra of SBS and SBS–Fu were shown on Figure S2.

2.3. The formation of the C_{60} crosslinked furan modified SBS films via Diels-Alder reaction

The SBS-20Fu was dissolved in toluene and then different contents of C_{60} were added into the SBS-20Fu solution. Then the mixture was stirred at about 80 °C for 6 h. After that, the solution was cast onto a glass dish and dried in an oven at 100 °C for 12 h. Different content of C_{60} was added according to the weight of SBS. The properties of the materials could be tuned by weight ratio of the C_{60} to SBS. Different hybrids with the addition of C_{60} including 0.1%, 0.3%, 0.5%, 1% and 2 wt% were obtained in the system. The samples were named in the form of SBS-20Fu-xC_{60}. “x” stood for the weight ratio of C_{60} to SBS.

2.4. Measurements

^{13}C NMR spectra were acquired by a Mercury Plus spectrometer (Varian, Inc., USA) operating at 400 MHz with toluene-d8 as the solvent and tetramethylsilane (TMS) as an internal standard at room temperature.

The UV–vis spectra of the samples were tested with a UV-2550 spectrophotometer (Shimadzu, Japan). The polymer aqueous solutions were prepared with 0.1 mg/mL copolymer concentration in toluene.

The morphology of the samples was examined by tapping-mode atomic force microscopy (TM-AFM). TM-AFM measurements were carried out in a SII Nanonavi E-sweep under ambient conditions. The measurements were performed using commercial Si cantilevers with a nominal spring constant and resonance frequency at about 40 N/m and 300 kHz, respectively (AFM Probes, NSC11).

The tensile test and cyclic tension test of the films was taken on