Self-assembled elastomer nanocomposites utilizing C60 and poly(styrene-b-butadiene-b-styrene) via thermally reversible Diels-Alder reaction with self-healing and remolding abilities

Jing Bai, Qing He, Zixing Shi, Ming Tian, Hongjie Xu, Xiaodong Ma, Jie Yin

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In this article, C60 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 C60 and even small amount of C60 could lead to great change in the morphologies of SBS. Three types of morphologies of SBS could be observed as the content of C60 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 C60 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 C60 possessed the self-healing and remolding abilities via retro-Diels-Alder (rDA) reaction. All in all, C60 could provide the multiple functions toward the modification of SBS via DA reaction.

1. Introduction

C60 is the most prominent representative of the fullerene family [1]. As one of important carbon based nanomaterials (Fullerene, carbon nanotubes and graphene), C60 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 C60 was based on the 1,3-dipolar cycloaddition; the reaction between N-methylglycine (sarcosine), formaldehyde, and C60 led to the N-methylpyrrolidine derivative [4,5] and photochemical treatment of triethylamine with C60 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 C60, it was an ideal dienophile for the Diels-Alder reaction. As reported, C60 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) 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 [16]. Therefore, C60 could react with this type macromolecular diene to construct C60 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’s 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...
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 C60 has strong physical interaction with PS block via π-σ conjugation [21]. However, in our system, C60 could be also co-assembled 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 polyurethane material 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 still a great challenge towards modification of SBS. In our research work, this kind of hybrid based on C60 and SBS-Fu via DA reaction could provide a balanced solution to these problems due to several following reasons: first, C60 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 C60 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 C60 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 C60 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 C60 and SBS-Fu at the molecular level for both chemical and physical interactions. Due to their chemical reaction via Diels–Alder, C60 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 C60. 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 C60 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 C60 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 1H NMR, FTIR and elemental analysis in our previous work. The 1H NMR spectra of SBS and SBS–Fu were shown on Figure S2.

2.3. The formation of the C60 crosslinked furan modified SBS films via Diels–Alder reaction

The SBS-20Fu was dissolved in toluene and then different contents of C60 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 C60 was added according to the weight of SBS. The properties of the materials could be tuned by weight ratio of the C60 to SBS. Different hybrids with the addition of C60 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-xC60. “x” stood for the weight ratio of C60 to SBS.

2.4. Measurements

13C 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
an Instron 4465 instrument at a crosshead speed of 100 mm/min at room temperature with the humidity of about 30%. Dumbbell specimens with width of 4 mm and length of 30 mm were cut from the cast films. Data analyses were based on five measurements on each sample performed at the same conditions. In the cyclic tension test, the samples were firstly stretched to 100% strain and then returned to their original state.

The dynamic mechanical tests were carried out on a (DMTA) (TA Q800, TA Instruments, USA) under the temperature range from 153 to 393 K. The frequency was fixed at 1.0 Hz and heating rate is 10 K/min.

The photos for self-healing process were obtained with VF-7510 (KEYENCE).

The gel fraction and swelling ratio of data were obtained by soaking the samples in toluene for 48 h at room temperature. Then the insoluble part of the sample was dried at 80°C to the constant weight (W3). The original weight of the sample was W1. The weight of the swollen sample immediately taken out of solvent was signed as W2. The gel fraction (GF) and the swelling ratio (SR) were calculated according to the follow two formulas.

\[
\text{GF} = \frac{W_3}{W_1} \times 100\%; \quad \text{SR} = \frac{W_2}{W_1}
\]

3. Results and discussion

3.1. Preparation of the composites based on SBS-Fu and C_{60}

Fig. 1 illustrated the process of fabrication of hybrids based on the SBS-20Fu and C_{60} of different contents from 0.1 to 2 wt % of SBS via solution cast method. As shown in Fig. 2B, it was found that the color of solution changed from purple (the color of C_{60} solution, Fig. 2A) to bordeaux when C_{60} was added into SBS-20Fu solution. However, the color of solution having SBS and C_{60} still remained purple. After evaporated at 80°C, the hybrid films with different color were obtained. As shown in Fig. 3B, the color of SBS-20Fu-xC_{60} series films were brown and the color of SBS-xC_{60} series still remained purple.

Such color difference would provide the direct evidence that different interaction could exist between SBS-20Fu and C_{60} with the presence of furan groups compared with the blends having pure SBS and C_{60}. Furthermore, the solubility of the hybrids film was characterized to demonstrate the interaction between the SBS-20Fu and C_{60}. As shown on Fig. 2C, it was found that the film of SBS-20Fu-2C_{60} would be only swollen in toluene without dissolution, while the blends of pure SBS with the same content of C_{60} could easily dissolve in toluene and this different solubility behaviors before and after blending with C_{60} indicated that C_{60} could really act as crosslinking agents toward SBS-20Fu via Diels-Alder reaction to form tri-dimensional polymer networks since the solubility of material were quite different in the state of network or linear structure [40].

3.2. Gel fraction and swelling ratio measurements

Gel fraction and swelling ratio of the materials could be utilized to further investigate the crosslinked structure. As shown on Fig. 3A, it was found that the gel fraction of the hybrids was increased with increasing C_{60} content, accompanied by decreased swelling ratio. For example, it was observed that the gel fraction and swelling degree were 63.8% and 10.03 respectively with incorporation of 0.1 wt% C_{60} (SBS-20Fu-0.1C_{60}). With increasing C_{60} content up to 2%, the gel fraction of the composite increased to 86.7% and the swelling ratio decreased to 6.23. Therefore, based on the above analysis, it was found that increasing crosslinkers (C_{60}) content would result in increased crosslinked degree, which finally increased the gel fraction and decreased the swelling ratio. Meanwhile, for the max value of gel fraction in this system was 86.7%, it meant that some fraction of the material was still linear and could be dissolved in solvent.

Based on the results from solubility of furan modified SBS after blending with C_{60}, it was concluded that C_{60} could be applied as dienophile crosslinking agents to build the inorganic-organic network for SBS-20Fu via DA reaction at the molecular level, which was firstly reported in elastomer based hybrids as far as we know.

![Fig. 1. The reaction between C_{60} and SBS-20Fu and the formation of the crosslinked structure of SBS-20Fu with C_{60}.](image-url)
3.3. $^{13}$C NMR and UV-Vis for the samples

To prove the DA reaction between furan groups on the modified SBS chains and C$_{60}$, the $^{13}$C NMR spectrum was first utilized to monitor the change of structure for C$_{60}$ and SBS-20Fu upon blending in toluene-d$_8$ before gelation. As shown in Fig. 4B, the $^{13}$C NMR spectrum of the SBS-20Fu exhibited the typical carbon atom signals attributed to the furan ring which was branched on to PB block of the SBS chains at 141.5 (a, d), 110.2 (c) and 105.9 (b) ppm for the carbon atom in the furan rings respectively. Meanwhile, the C$_{60}$ showed typical peak at 142.8 ppm [41]. After the reaction, these signals almost disappeared and the new peaks appeared around 140–143 (f) ppm. These new signals could be explained with the formation of new conjugation structure from the furan and C$_{60}$ via DA reaction. Therefore, the result of $^{13}$C NMR could also prove the DA reaction between C$_{60}$ and furan groups on the polymer chains.

Fig. 2. (A) solution of C$_{60}$ in toluene (B) photos of the solution of SBS-2C$_{60}$ and SBS-20Fu-2C$_{60}$ from left to right (C) photo of the samples in toluene (SBS-2C$_{60}$ and SBS-20Fu-2C$_{60}$ from left to right).

Fig. 3. (A) Gel fraction and the swelling ratio of the series materials (B) The picture of the SBS-0.3C$_{60}$ and SBS-20Fu-0.3C$_{60}$ from left to right.

Fig. 4. (A) UV-Vis spectrum of the samples (B) $^{13}$C NMR spectrum of the samples.
UV-vis spectra were also taken for measuring the structure variation for the blends of C60 and SBS. As shown on Fig. 4A, for the curve of C60, due to the conjugated structure of C60, there were two peaks at 283 and 336 cm$^{-1}$ for the electronic transition of $\pi-\pi^*$ and $n-\pi^*$ [42]. Then after reacting with the furan modified SBS, the primary conjugated structure of C60 was destroyed for the DA reaction with furan groups on the polymer chains, and the peak at 336 cm$^{-1}$ disappeared. Therefore, for the new structure of the product also was conjugated structure, the peak at 283 cm$^{-1}$ existed still but broadened for the new structure. Meanwhile, the change of the peak could be explained with different electronic energy level between C60 and the product. This phenomenon could prove the reaction between C60 and furan groups on the polymer chains.

3.4. Morphologies for the SBS-20Fu-xC60 and SBS-xC60 series materials

As we know that inner morphology was a very important factor for determining the final mechanical properties [43], and it has been reported that the addition of nanoparticles or crosslinkers can change the morphologies of the block polymer [44,45]. Hence, it was necessary to investigate its morphological variation before and after co-assembly with C60 via DA reaction. Since AFM could detect PB and PS phases based on their different hardness and the bright region represented the hard phase (PS phase) and the dark region stood for the soft phase (PB phase), AFM measurements is especially suitable for characterizing the change for morphologies of the block polymers on their phase diagrams.

Fig. 5 showed the morphology of the pure SBS. It was found that PS domains acted as cylinders dispersed in the PB matrix. Therefore, PS domains were dispersed phase and PB domains were the continuous phase since only 30 wt% PS block was in the SBS copolymers. After 20% furan groups attached onto the PB block through thiol-ene reaction, great changes were found for the morphologies of the hybrids. As shown in Fig. 5, both PB and PS phases were acted as continuous phases in its morphology, indicating that the presence of attached furan groups in PB phase had affected the interaction toward PS chains so that the physical crosslinking introduced by the vitrification of PS domains was partly destroyed and the PS domains had transferred from dispersed phase to continuous phase. With the presence of C60, the morphologies of SBS were further changed via Diels-Alder reaction taking place between C60 and furan groups attached onto the PB block of SBS. As shown in Fig. 5 with the presence of 0.1 wt% C60, the PB phase aggregated together to form dots surrounded by PS domains to form honeycomb like morphologies and the diameter of dots for PB phase was located at about 40 nm and the width of PS around PB phase was observed at about 15 nm. When the C60 content was increased to 0.3 wt%, the honeycomb like structure was gradually destroyed and bi-continuous phase morphology began to appear. Further increasing content of C60 above 0.5 wt%, both PB and PS phase were combined together to form worm-like bi-continuous phase and the width of both PB and PS phase was progressively decreased from 20 to 15 nm, 15 to 10 nm, respectively, as the content of C60 was increased from 0.5 to 2 wt%. Therefore, based on the analysis of morphological variation for C60 in SBS matrix via DA reaction, it was found that Diels-Alder reaction between C60 and furan modified PB block play a profound effects on the morphologies for SBS hybrids. Since the reaction occurred only in the PB phase, the transition of PB phase would finally influence the interaction between PB and PS phase and the morphologies of the composites could be tailored by the co-assembly of SBS and C60 in the different contents. However, different morphologies were obtained for the blends with the pure SBS and C60 in the absence of DA reaction in PB phase. Since C60 could have only physical interaction with PS phase via $\pi-\pi^*$ effect, the incorporation of C60 could have more influence on PS phase than PB phase. Therefore, cylinders like PB phase could gradually change into dot like dispersed domains as the content of C60 was increased from 0.1 to 0.5 wt%. Further increasing content of C60 could totally destroyed initial dispersed PS phase to form the continuous phase structure.
and PB phase could also be observed to form spot like structure with diameter located around 30 nm as content of C60 was about 2 wt%.

Therefore, based on the comparison of these blends of SBS and C60 via different interaction, they showed quite different morphologies. As previously reported, the increase crosslinking density led to the change of the morphologies of the block polymer [16,29,46]. With Diels–Alder reaction between C60 and PB phase for SBS-20Fu-xC60 series, the morphologies of hybrids via assembly could gradually change from honeycomb like structure to wormlike bi-continuous phase structure. However, with the π-π physical interaction between C60 and PS phase for SBS-xC60, the dispersed PS domains gradually disappear to form bio-continuous phase structure with aggregation of C60 observed. All in all, different morphologies and interaction could finally reflect in the different mechanical properties of SBS.

3.5. The mechanical properties of SBS-20Fu-xC60 and SBS-xC60 series hybrids

Since the mechanical properties of materials has closely relationship with their morphologies [47,48] and crosslinking density, it was necessary to investigate the different influential effect on mechanical properties of physical blending hybrids for physical (π-π) and the chemical crosslinked hybrids via chemical interaction (DA reaction) interaction between furan modified SBS and different contents of C60.

Fig. 6 were typical stress-strain curves for these two different series (SBS-20Fu-xC60 and SBS-xC60) and their tensile stress at 300%, 500% and 700% were summarized on Fig. 6C and D. It was generally found that incorporation of C60 could improve the mechanical properties for SBS via the physical or chemical interaction and increasing content of C60 could progressively improve the tensile strength. However, comparison of these two kinds of blends in detail could prove that the reinforcement on chemical modes via DA reaction was much more efficient than that on the physical modes via π-π interaction. For example, with the presence of 0.1 wt % C60, the tensile strength and strain at break for SBS-20Fu-0.1C60 were observed at 14.82 MPa and 977.34% respectively, almost 8.5 times increase in tensile strength as compared with the pure SBS. However, SBS-0.1C60 only showed the tensile strength and strain at break at 2.83 MPa, 1270.8% respectively, only 1.64 times increase in tensile strength as compared with the pure SBS. When the content of C60 was increased up to 2 wt%, the tensile strength at break was 19.84 MPa and tensile strain at break decreased to 589.85% for SBS-20Fu-2C60. However, the tensile strength for SBS-2C60 was only 3.98 MPa with tensile strain at break at 945.6%. In the meantime, the data obtained from tensile strengths at the elongation of 100, 300, and 500% also vividly support the same phenomena that C60 could be acted as effective additive to reinforce the mechanical properties of furan modified SBS and chemical interaction via DA reaction could exhibit much more reinforced effect toward the SBS than that based on physical interaction. Meanwhile, the results of tensile test also proved that the more C60 (crosslinker) was added the higher of strength and the lower of the elongation at break. The mechanical properties of the materials can be affected with the crosslinking density and inner structure.

![Fig. 6.](image) (A) Stress–strain curves of SBS-20Fu-xC60 hybrids (B) Stress–strain curves of SBS-xC60 hybrids (C) Tensile stress at elongation of 100%, 300%, and 500% of SBS-20Fu-xC60 hybrids (D) Tensile stress at elongation of 100%, 300%, and 500% of SBS-xC60 hybrids.
3.6. Dynamic mechanical analysis of the SBS-20Fu-xC60 series materials

Dynamic mechanical analysis was further utilized in tensile mode in order to observe the thermomechanical properties for the blends of SBS-20Fu-xC60. The modulus and dissipation factor (tanδ) curves were shown on Fig. 7 and the data was summarized in Table S3. For the SBS-20Fu-xC60 series materials, it was found that the storage modulus at room temperature was increased by increasing content of C60. For example, the storage modulus at room temperature could be improved from 10.5 MPa for the sample of SBS-20Fu-0.1C60 to 78.25 MPa with C60 content increased to 2% and almost 8.7 times increase as compared with that for pure SBS. The results from DMA analysis were in agreement with that from stress-strain measurements.

The plots of tan δ of SBS-20Fu-xC60 series of composites were exhibited in Fig. 7B, and the DMA data was summarized in Table S3. As shown on Fig. 7B, similar with the pure SBS, SBS-20Fu-xC60 series of composites possessed two characteristic relaxation processes [47,49]. One was at low temperature (about -80--65 °C) and it was related to the glass-transition temperature (Tg) of the PB block (Tg1). The other one was at about 70--85 °C belonged to Tg of PS (Tg2). For the furan branched SBS, when C60 was added, the position of Tg1 for PB phase moved toward higher temperature, while the position of Tg2 which belonged to PS phase was shifted towards lower temperature. It could be explained with the formation of the crosslinking structure via DA reaction between C60 and furan groups on the polymer chains. The crosslinking structure resulted in the restriction of the chains movement in PB phase for the crosslinking reaction happened in this phase. Therefore, the Tg of PB phase moved towards high temperatures compared with pure SBS. While for the PS domains, the plasticization of PS phase by PB phase lead the Tg of PS phase moved towards low temperature. When the addition of C60 increased, the crosslinking density increased and the magnitude of these shifts of Tg became more remarkable.

3.7. Resilience properties of the SBS-20Fu-xC60 series composites

Elastic resilience was a very important property for elastomer materials, which was a shortcoming for the SBS with thermoplastic character. Due to physical crosslinking structure in SBS copolymer, SBS copolymers usually show poor behavior in size stability and low elastic resilience. In this paper, we used C60 as an effective inorganic chemical crosslinking agent to build the network toward furan modified SBS elastomer. In this way, elastic resilience could be enhanced. The cyclic tension test was taken to characterize their elastic resilience properties the two series of hybrids (SBS-20Fu-xC60 and SBS-xC60 series) co-assembly with C60. Fig. 8 demonstrated cyclic tensile stress-strain curves of SBS-20Fu-xC60 series materials and the control samples (SBS-xC60). The samples were firstly stretched to 100% strain and then returned to their original state. As shown in Fig. 8, the hybrids based on Diels-Alder reaction (SBS-20Fu-xC60) all showed good resilience and all the samples could return to original length without noticeable residual strain. While the samples based on the direct blending (SBS-xC60 series) cannot return to the original length and all the SBS-xC60 series samples possessed residual strain about 20%, which was still similar to the pure SBS without the presence of C60. Difference in elastic resilience could come from the different interaction between C60 and polymer. For the SBS-20Fu-xC60 series materials, chemical crosslinked network between C60 and polymer matrix via Diels-Alder reaction insured the effective loading transfer from the polymer matrix to C60, which finally improved the mechanical and resilience properties greatly. However, via direct blending method, the improved interaction between C60 and pure SBS was only a physical effect between C60 and PS block of the copolymer and this new physical crosslinking could not effectively improve the interface action between PB and PS phase for pure SBS.

3.8. Thermal recyclability and self-healing property of the chemical crosslinked hybrids via DA reaction

Since thermoplastic SBS is usually poor in solvent resistance and Elastic resilience, people usually incorporate the network into SBS to improve above two poor properties, which usually sacrifice its remolding ability, one of important properties for SBS. Therefore, the balance between remolding ability and improved solvent resistance is usually great challenge for modification of SBS. In this paper, the solvent resistance and elastic resilience have been greatly improved by using C60 as dynamical crosslinker toward furan modified SBS elastomer. Since the crosslinking reaction was based on thermally reversible DA reaction, this kind of nanocomposites could be remolded based on rDA reaction at high temperature. In this way, the thermal plastic behavior still maintained for the hybrids. In this study, two methods were used for evaluating the remolding behaviors. One was sol-gel method and the other was to remold materials under thermal treatment.
The sol-gel experiment was firstly taken for the SBS-20Fu-0.3C60 (the typical example) to prove the reversibility of the crosslinked network and the recycle ability of the materials. As shown in Fig. 9C, when the temperature was higher than 180 °C, the crosslinked SBS-20Fu could gradually dissolve in dichlorobenzene with a solution obtained and this phenomena indicated that the disconnection of DA linkage via the rDA reaction at high temperature could liberate the chains of polymer from network to give...
them remolding behavior [38,50]. However, as the temperature went down, the chemical crosslinking linkage via DA reaction was recovered again and the homogenous gel was formed as shown on Fig. 9C. Furthermore, we did this sol-gel experiment with the sample of SBS-20Fu-0.3%C₆₀ for three times and the same phenomenon was observed, which proved that the crosslinked SBS could be thermally reversible sol-gel for at least three times.

In the second way of proving the recycle ability, the thermally remolding experiment was taken on the broken material. The film (SBS-20Fu-0.3%C₆₀) was firstly cut into small pieces and then remolded under the pressure of 10 kPa for 5 min at 190 °C. After that, a solid polymer film was fabricated again. This test was also repeated for 3 times. To estimate the effect of remolding process on the mechanical properties of the materials, the tensile test of the remolded samples was taken after 1 day settled at room temperature. As shown on Fig. 9B, after three remolding processes, both tensile strength and strain of the sample were still kept at 7.7 MPa and 681%. The decrease of mechanical properties as compared with original sample might be attributed to thermal oxidation degradation during the remolding process under high temperature.

Due to the reversibility of the crosslinked network via DA reaction, it was also found that the crosslinked hybrids showed good self-healing property (Fig. 10). The film was firstly cut with a surgical blade and formed a crack on it. As shown on Fig. 10, the crack was about 25 μm. When the sample was heated to about 180 °C and kept at the temperature for about 10 min, the crack gradually decreased and disappeared with a scar left. The liberated chains from crosslinked structure via rDA reaction at high temperature could move together and the crack could be healed via DA reaction when the temperature went down. Therefore, the co-assembly of C₆₀ and furan modified SBS via DA reaction at the molecular level provided the special morphologies for furan modified SBS with great improved mechanical properties, recycling and self-healing abilities.

4. Conclusion

In conclusion, the hybrid system was produced based on the co-assembly of C₆₀ and furan modified SBS via Diels-Alder reaction, where C₆₀ was acted as “dienophile” and SBS-20Fu was used as “macromolecular diene”. The reaction between them was confirmed by the spectra analysis including UV spectra and ¹³C NMR. Based on the assembly via the chemical interaction between C₆₀ and PB block in SBS at the molecular level, the morphologies of the hybrids could be adjusted by the content of C₆₀ and crosslinked network was established between C₆₀ and the furan modified SBS. In this way, the final assembly structure would substantially increase the properties for the hybrids, including the solvent resistance, elastic resilience and tensile strength. With the presence of 2 wt% C₆₀, the strength could be observed at 19.84 MPa, almost 14 times increased compared with pure SBS. Meanwhile, for the chemical crosslinking caused by DA reaction was reversible at high temperature, the hybrids possessed the self-healing and remolding abilities via rDA reaction. This type of hybrid provided a typical model for keeping the balance between the recycling ability and crosslinked structure.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2017.03.080.

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