Novel blends of acrylonitrile butadiene rubber and polyurethane-silica hybrid networks

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Received 23 November 2011; accepted in revised form 31 January 2012

Abstract. Novel blends of acrylonitrile butadiene rubber (NBR) and polyurethane-silica (PU-SiO₂) hybrid networks have been prepared by melt blending. The PU-SiO₂ hybrid networks were formed via the reaction of NCO groups of NCO-terminated PU prepolymer and OH groups of SiO₂ in the absence of an external crosslinking agent (i.e. alcohols and amines) during the curing process of NBR. Both in the neat PU-SiO₂ system and the NBR/(PU-SiO₂) system, the NCO-terminated PU prepolymer could be crosslinked by SiO₂ to form PU-SiO₂ hybrid networks. The effects of PU-SiO₂ introduction into the NBR, on the properties of the resulting blends were studied. It was found that the vulcanization was activated by the incorporation of PU-SiO₂. Transmission electronic microscopy (TEM) studies indicated that the interpenetration and entanglement structures between NBR and PU-SiO₂ increased with increasing PU-SiO₂ content and the quasi-interpenetrating polymer networks (quasi-IPN) structures were formed when the PU-SiO₂ was 50 wt% in the NBR/(PU-SiO₂) systems. The microstructures formed in the blends led to good compatibility between NBR and PU-SiO₂ and significantly improved the mechanical properties, abrasion resistance and flex-fatigue life of the blends.

Keywords: polymer blends and alloys, acrylonitrile butadiene rubber, polyurethane, silica, hybrid materials

1. Introduction

Polymer blends have been of great interest particularly in the last two decades or so. The factors that have fueled this interest are cost and time associated with the development of new polymers and the ability to tailor properties by blending, which may result in new, desirable and, in some cases, unexpected synergistic effects on the properties [1, 2]. Acrylonitrile butadiene rubber (NBR) possesses attractive properties, such as good oil resistance, abrasion resistance, elastic properties and low gas permeability, and is widely applied in a wide range of industrial equipment. However, the mechanical properties, ozone resistance and processibility of NBR are poor [3]. Fillers such as silica, carbon and clay are usually added to improve its mechanical

strength [4–7]. However, the addition of fillers has some limitations and desired properties cannot be achieved. The blending of NBR with another polymer can overcome these limitations.

Polyurethane (PU) is applied in many different fields because of its excellent properties, including its high tensile modulus, abrasion resistance, tear resistance, chemical resistance, low-temperature elasticity as well as ease of processing [8, 9]. The favorable properties of PU have raised interest in preparing NBR/PU blends, which can bring to NBR the valuable properties of PU, especially the high strength and excellent abrasion resistance. The applications of different forms of PU in NBR have been reported. Direct blending hydrothermal decomposed crosslinked PU (HD-PUR) or thermoplastic

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PU (TPU) with NBR can obtain NBR/PU blends [10–12]. However, these blends generally exhibit poor mechanical properties because of incompatibility and phase separation of the initial components. In order to minimize phase separation and increase interfacial adhesion, compatilizers usually are used for these systems, but this would lead to the increased cost and entail the use of complicated procedures. Dynamically cured TPU and NBR blends were prepared by Tang *et al.* [13]. They reported that the mechanical properties for these NBR/TPU dynamically cured blends were much better than those for NBR/TPU simple blend systems. However, in the NBR/TPU blends, the TPU phase is linear structure, not a crosslinked network, which restricts further properties improvement of the blends. The blends of NBR and PU ionomers were prepared by Dimitrievski *et al.* [14]. They studied the influence of the PU ionomers on the blend properties, blend miscibility and on the course and kinetics of vulcanization. In addition, blends of NBR and in-situ produced PU have been studied. Karger-Kocsis *et al.* [15, 16] prepared rubber blends of hydrogenated nitrile rubber (HNBR) and PU, in which the crosslinked PU was formed from solid PU precursors, viz. polyol and blocked polyisocyanate, during curing of the HNBR rubber. The mechanical and tribological properties of the blends were researched. PU/NBR blends were prepared by Desai *et al.* [17] through a combination of solution blending and mastication process. However, the use of large quantity of organic solvents and complicated procedures limited the application of the method. In this work, novel blends of NBR and in-situ produced PU-silica (PU-SiO₂) hybrid networks are prepared. The NCO-terminated PU prepolymer is firstly prepared, the silica (SiO₂) bearing numerous silanol groups is subsequently introduced, then the mixture of PU prepolymer and SiO₂ is dispersed in NBR matrix during the mixing process. The PU-SiO₂ hybrid networks are formed via the reaction of NCO groups of NCO-terminated PU prepolymer and OH groups of SiO₂ during the curing process of NBR. This process has not yet been reported in the literature. In this approach, the mixture of PU prepolymer and SiO₂ is in a gel-like form, which is strongly favored in solid phase raw rubber compounding. It could be pointed out that the SiO₂ in the mixture acts as not only as a reinforcing agent but

also a crosslinking agent of the PU prepolymer. Compared with the traditional crosslinking agent [18, 19], such as trimethylpropane (TMP) and 4,4'-methylenebis-(2-chloroaniline) (MOCA), the crosslinking agent used in this work is economic and environmentally friendly.

The aim of this work was to prepare blends of NBR and in-situ produced PU-SiO₂ hybrid networks. The structures of the PU-SiO₂ hybrid materials and NBR/(PU-SiO₂) blends were characterized by Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC) and transmission electronic microscopy (TEM). The effects of PU-SiO₂ content on the vulcanization, compatibility, mechanical properties, abrasion resistance and flex-fatigue life of the blends were studied.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI) from Bayer (Germany) was purified by vacuum distillation. Poly(tetramethylene glycol) (PTMG, $M_n = 1000$ g/mol) from Mitsui (Japan) and dibutyltin dilaurate (DBTDL, as catalyst) from Shanghai Reagent Co., (Shanghai, China) were dried at 80°C under vacuum (10mmHg) for 8 h before use. The NBR with acrylonitrile content 26% was kindly provided by Japan Synthetic Rubber Company. Tetramethyl thiuram disulfide (TMTD), 2,2'-dibenzothiazole disulfide (DM), zinc oxide (ZnO), stearic acid (SA) and sulfur (S) were obtained from Kemai Chemical Technical Co. Ltd. (Tianjin, China). Precipitated silica bearing surface silanol groups was purchased from Huiming Chemical Technical Co. Ltd. (Jiangxi, China). The surface area and primary particle size are 210 m²/g and 20 nm respectively.

2.2. Preparation of the mixture of PU prepolymer and SiO₂

Weighed amounts of PTMG and DBTDL (0.05 wt% based on PUs) were charged into a round-bottomed flask, heated until 85°C, and thoroughly mixed with a predetermined amount of IPDI, which corresponded to a fixed NCO/OH ratio of 2:1. The reaction system was stirred vigorously with mechanical stirring, under a dry nitrogen atmosphere. The completion of the reaction was determined by the di-n-butylamine titration method when the theoretical

NCO percentage was reached. Then, the NCO-terminated PU prepolymer was obtained. After the PU prepolymer had cooled to room temperature, calculated amounts of SiO₂ (30 wt% based on PU prepolymer) was added, and the mixture was stirred at room temperature until it turn into gel-like form (for about 10 min), then the mixture of PU prepolymer and SiO₂ was obtained.

2.3. Preparation of blends of NBR and PU-SiO₂ hybrid networks

A two-roll mill (Kesheng Co. Ltd. Guangzhou, China) was used to prepare the NBR/(PU-SiO₂) compounds. First, NBR and additives were mixed at room temperature for about 7 min, and then the calculated amounts of mixture of PU prepolymer and SiO₂ was added to the NBR compounds. The NBR compounds and mixture of PU prepolymer and SiO₂ were mixed uniformly at room temperature for about 5 min, then the NBR/(PU-SiO₂) compounds were vulcanized in a standard mold at 120°C for optimal cure time (*t*₉₀), which was determined by the U-CAN UR-2030 vulcameter (Taiwan, China). During the curing of the NBR/(PU-SiO₂) compounds, the NCO groups of PU prepolymer reacted with OH groups of SiO₂ and the PU-SiO₂ hybrid networks were produced, and the linear molecular chains of NBR were crosslinked into three-dimensional networks under the action of the vulcanization system. Therefore, the blends based on NBR and PU-SiO₂ hybrid networks were generated. Figure 1 shows the schematic reaction of PU prepolymer and SiO₂. In the present study, the recipe for NBR system was as follows (phr): NBR 100; ZnO 5; stearic acid 1.5, sulfur 1.5; TMTD 0.3; DM 1.5. The weight content of mixture of PU prepolymer and SiO₂ were 10, 20, 30, 40 and 50% in the NBR/(PU-SiO₂) blends, which were regarded as NBR/(PU-

SiO₂)-10, NBR/(PU-SiO₂)-20, NBR/(PU-SiO₂)-30, NBR/(PU-SiO₂)-40 and NBR/(PU-SiO₂)-50, respectively. For comparison purposes, neat NBR and PU-SiO₂ sheets were also produced at 120°C using appropriate respective optimum cure times. Specimens for the investigations were cut from the compression molded sheets of ca. 2 mm thickness.

2.4. Characterization

Fourier-transform infrared (FTIR) spectroscopy was conducted on a Nicolet Fourier-transform infrared spectrophotometer (Thermo Nicolet Corporation, Nicoletis10, America) at a resolution of 4 cm⁻¹. PU prepolymer and SiO₂ were tested by transmission mode; PU-SiO₂ hybrid materials, NBR vulcanizate and NBR/(PU-SiO₂)-50 blend were tested by attenuated total reflection mode.

X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, England) was performed to reveal the reaction between PU prepolymer and SiO₂. SiO₂, PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend were tested with a monochromated Aluminum K α source (1486.6 eV). All XPS spectra were calibrated to its reference C1s component at 285.0 eV [20]. The PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend were treated with butanone extraction and dried at 80°C for XPS test. The unreacted NCO-terminated PU prepolymer and SiO₂ should be removed by butanone extraction; otherwise they would interfere with the XPS results.

The isothermal curing process of the NBR, mixture of PU prepolymer and SiO₂ and NBR/(PU-SiO₂)-50 compound were assessed by differential scanning calorimetry (DSC). The measurements were performed on a TA Q20 (New Castle, America) under N₂ atmosphere. The aluminum pans containing the samples were inserted onto the DSC sensor at 120°C and left at 120°C for 200 min.

Vulcanization parameters and curing curve for NBR, PU-SiO₂ and NBR/PU-SiO₂ compounds were tested in an oscillating disk rheometer (ODR) according to ASTM D2084 using a U-CAN UR2030 vulcameter. The temperature was set at 120°C, with a rotation amplitude of 1°. The compounds were tested under pressure in the die cavity located in the electrically heated plates. The cavity was formed by a fixed lower die and a movable upper die. The ODR maintained a contact with the specimen until the cure reaction was completed.

Figure 1. The schematic reaction of PU prepolymer and SiO₂

The specimens were ultramicrotomed into thin pieces of about 120 nm thickness with a Leica EM UC6 (Wetzlar, Germany). Then the TEM observations were carried out using a Philips Tecnai 12 TEM (Amsterdam, Netherlands) at an accelerating voltage of 30 kV.

Dynamic Mechanical Analysis (DMA) spectra of the samples were obtained by using EPLEXOR @ 500 N/1500 N advanced dynamic mechanical spectrometer (GABO Company, Germany). The specimens were analyzed in tensile mode at a constant frequency of 10 Hz and a strain of 0.5%, and scanned from -100 to 100°C at a heating rate of $3^{\circ}\text{C}/\text{min}$.

The tensile and tear tests of the vulcanizates were performed according to ASTM D412 and ASTM D624 specifications, respectively. U-CAN UT-2060 (Taipei, Taiwan) instrument was used with the crosshead speed of 500 mm/min. Shore A hardness was performed following ASTM D2240 using Sanling XY-1 sclerometer (Shanghai, China).

Akron abrasion loss was evaluated by a Gotech GT-7012-A testing machine (Taipei, China) according to BS 903/A9. The flex-fatigue life was measured using a De Mattia GT-7011-D flexing machine (Taipei, China) according to ASTM D430. For each sample, three pieces were tested and the average flex-fatigue-life value was reported. The flex-fatigue life was defined by the cycles at which a visible crack, that is, a grade-one crack, appeared.

3. Results and discussion

3.1. Structure characterization of PU-SiO₂

hybrid materials and NBR/(PU-SiO₂) blend

3.1.1. Fourier-transform infrared spectroscopy analysis

The FTIR spectra of the NCO-terminated PU prepolymer, SiO₂, PU-SiO₂ hybrid materials, NBR vulcanizate and NBR/(PU-SiO₂)-50 blend are shown in Figure 2. The spectrum of the NCO-terminated PU prepolymer shows absorption peak at 2266 cm^{-1} corresponding to the NCO group. The characteristic peaks of urethane group are observed at 3326 and 1714 cm^{-1} , corresponding to stretching vibrations of N-H and C=O groups, respectively. For the SiO₂, the absorption peaks at 1094 and 800 cm^{-1} are associated with Si-O-Si asymmetrical and symmetrical stretching vibrations respectively, and the absorption peaks at 3446 and 960 cm^{-1} represent the

Figure 2. FTIR spectra of (a) NCO-terminated PU prepolymer, (b) SiO₂, (c) PU-SiO₂ hybrid materials, (d) NBR vulcanizate and (e) NBR/(PU-SiO₂)-50 blend

Figure 3. FTIR spectra of the NCO-terminated PU prepolymer, SiO₂, PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend in the region of 1800 – 4000 cm^{-1}

Si-OH stretching vibrations. The spectrum of NBR vulcanizate shows absorption peak at 2236 cm^{-1} corresponding to the $-\text{CN}$ group. The $-\text{CH}_2$ (2917 and 2847 cm^{-1}), the *trans* $>\text{C}=\text{CH}-$ (962 cm^{-1}) and the vinylidene ($>\text{C}=\text{CH}_2$; 910 cm^{-1}) are assigned to the NBR backbone. FTIR spectra of NCO-terminated PU prepolymer, SiO₂, PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend in the region of 1800 – 4000 cm^{-1} are reported in Figure 3. As shown in Figure 3, the absorption peaks of NCO at 2266 cm^{-1} and Si-OH at 3446 cm^{-1} in PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend disappear. FTIR spectra of the SiO₂, PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend in the region of 600 – 1200 cm^{-1} are shown in Figure 4 and the integration results of Si-OH (960 cm^{-1}) and Si-O-Si

Figure 4. FTIR spectra of the SiO₂, PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend in the region of 600–1200 cm⁻¹

Table 1. Integration results of Si–OH and Si–O–Si in SiO₂ and PU-SiO₂ hybrid materials

	Si–OH (960 cm ⁻¹)	Si–O–Si (800 cm ⁻¹)	I _(Si–OH) /I _(Si–O–Si)
SiO ₂	–3.24	–9.40	0.35
PU-SiO ₂	–0.48	–7.47	0.06

(800 cm⁻¹) in SiO₂ and PU-SiO₂ hybrid materials are reported in Table 1. For PU-SiO₂ hybrid materials, the intensity ratio of I_(960, Si–OH) to I_(800, Si–O–Si) is obviously decreased from 35% for SiO₂ to 6% with a decrement about 29%. The adsorption peak of Si–OH bonds (960 cm⁻¹) overlaps with the *trans* >C=CH– bonds (962 cm⁻¹) in NBR/(PU-SiO₂)-50 blend, while a weak absorption peak at 1080 cm⁻¹

appears, corresponding to the Si–O–C bonds, and overlaps with C–O–C and Si–O–Si absorption peaks, which also appears in the PU-SiO₂ hybrid materials. All these changes indicate that the NCO groups of PU prepolymer have reacted with the OH groups of SiO₂ in the neat PU-SiO₂ system and NBR/(PU-SiO₂)-50 system.

3.1.2. X-ray photoelectron spectroscopy analysis

The low-resolution XPS spectra of the SiO₂ and PU-SiO₂ hybrid materials are shown in Figure 5. As illustrated in Figure 5a, XPS survey spectrum of SiO₂ shows the carbon peak at 285.1 eV, oxygen peak at 532.1 eV and silicon peak at 103.3 eV [21]. While in the Figure 5b, besides these peaks in SiO₂, a new peak at 400.0 eV appears, which is attributed to the nitrogen atom. Table 2 summarizes the characteristic XPS data. It can be seen that the ratios of C/Si and O/Si in PU-SiO₂ hybrid materials increase compared with those in SiO₂. All the results can be explained by the fact that the PU prepolymer reacting with SiO₂ introduces abundance carbon atoms, oxygen atoms and nitrogen atoms onto the surface of SiO₂. The results demonstrate that the NCO groups of PU prepolymer have reacted with the OH groups of SiO₂. The high-resolution XPS spectra of Si 2p in SiO₂, PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend are reported in Figure 6. It can be seen that the binding energy (BE) of Si 2p in SiO₂ is located at 103.3 eV, while the BE shifts to a lower value in PU-SiO₂ hybrid materials and NBR/(PU-

Figure 5. XPS spectra of (a) SiO₂ and (b) PU-SiO₂ hybrid materials

Table 2. XPS atomic content for the SiO₂ and PU-SiO₂ hybrid materials

Samples	Atom	C [%]	O [%]	Si [%]	N [%]	C/Si	O/Si
SiO ₂		47.44	38.29	14.27	0	3.32	2.68
PU-SiO ₂ hybrid materials		64.99	25.70	7.01	2.30	9.27	3.67

Figure 6. XPS spectra of Si 2p in SiO₂, PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend

SiO₂)-50 blend. This means that the chemical environments of Si atoms in PU-SiO₂ hybrid materials and NBR/(PU-SiO₂)-50 blend have changed, which is mostly caused by the reaction of NCO groups of PU prepolymer and OH groups of SiO₂.

3.1.3. Differential scanning calorimetry analysis

Figure 7 shows plots of the reaction heat as a function of time for NBR, mixture of PU prepolymer and SiO₂ and NBR/(PU-SiO₂)-50 compound during isothermal curing at 120°C. As can be seen, DSC diagram of neat NBR exhibits an exothermic peak, which achieves a maximum at 76.1 min. This exothermic peak is attributed to the crosslinking reaction of NBR molecular chains in the presence of curing agent. DSC trace of mixture of PU prepolymer and SiO₂ shows an exothermic peak with a maximum at 6.5 min. This exothermic peak is due to the reaction of NCO groups of PU prepolymer

Figure 7. Curing time dependence of the heat flow during isothermal curing for NBR, mixture of PU prepolymer and SiO₂ and NBR/(PU-SiO₂)-50 compound at curing temperatures of 120°C

and OH groups of SiO₂. As for the NBR/(PU-SiO₂)-50 compound, two exothermic peaks are observed: the exothermic peak with a maximum at 3.1 min and the one with a maximum at 28.9 min. The former is attributed to the reaction of NCO groups and OH groups and the latter to the crosslinking reaction of NBR. This indicates that in the NBR/(PU-SiO₂)-50 compound, both the NBR system and PU-SiO₂ system are cured successfully. From Figure 7, it can be seen that both the reaction peak times of NBR system and PU-SiO₂ system in the NBR/(PU-SiO₂)-50 compound are reduced compared with those in the initial components. As for the NBR system in the NBR/(PU-SiO₂)-50 compound, the reaction peak time is 28.9 min, which shows a decrease of 62% compared with that of neat NBR. This is possibly caused by two aspects, on one hand, the organic zinc compounds (produced by ZnO with accelerating agent, i.e. DM and TMTD, during the vulcanization of NBR) and TMTD (containing tertiary amine groups) in the NBR system have catalytic action on the NCO/OH reaction of PU-SiO₂ system [19]; on the other hand, the urethane groups (containing secondary amine functionalities) which are produced by NCO groups with OH groups in the PU-SiO₂ system have an accelerating effect on the vulcanization of NBR. The secondary amine functionalities form complexes with accelerator compounds, which promote the crosslinking reaction of NBR. Similar accelerating effects have been reported by Karger-Kocsis and coworkers [10, 22, 23]. Because of the mutual cure accelerating effects of NBR system and PU-SiO₂ system, the reaction peak times of NBR system and PU-SiO₂ system in the NBR/(PU-SiO₂)-50 compound are reduced.

3.1.4. Morphology

Figure 8a and 8b show the TEM images of NBR/(PU-SiO₂)-30 blend and NBR/(PU-SiO₂)-50 blend, respectively. In the images, the gray and white phases represent NBR and PU, respectively, and the black aggregates dispersed within the PU are silica. As shown in Figure 8a, when the PU-SiO₂ weight content is 30% in the blend, a sea-island morphology is formed. The PU appears as the disperse phase and NBR presents as the continuous phase. The average dimension of the PU phase is 0.3~1.0 μm. As the PU-SiO₂ weight content increases to 50%, the NBR and PU show co-continuous morphology. As can be

Figure 8. TEM images of (a) NBR/(PU-SiO₂)-30 blend and (b) NBR/(PU-SiO₂)-50 blend

seen in Figure 8b, the structures formed in this blend are on the micrometer scale instead of the nanoscale (or molecular scale), which are more like quasi-interpenetrating polymer network (quasi-IPN). Similar results have been reported by Šebenik *et al.* [16]. The unique microstructures formed in the systems are beneficial to the improvement of compatibility between the two phases and enhancement of mechanical properties of NBR [16, 24], which will be illustrated below.

One may notice that the phase dimension in the blends is slightly large. This is because that the high molecular weight of the NBR leads to increased viscosity, which restrains the completely interpenetration between NBR and PU networks and the formation of fine structures. According to the method, silica is co-cured with PU and forms an independent network penetrated in the NBR network and there would be no chemical linkages between NBR

and silica, therefore, the silica is restricted in the PU phase and no any discernible silica can be seen in the NBR phase. From the images it can be seen that some silica aggregates in the PU phase, which is mostly because that the high viscosity of PU prepolymer restrains the fine dispersion of silica in the process of blending.

3.1.5. The formation of NBR/(PU-SiO₂) blends

From the above structure analysis, we propose the formation process of NBR/(PU-SiO₂) blends, as shown in Figure 9. First, the NBR gum and mixture of PU prepolymer and SiO₂ are mixed by melt blending. Under the strong shear force of the blending process, the low molecular weight PU prepolymer and SiO₂ can be easily mixed uniformly with NBR gum. In the process, the PU prepolymer molecular chains will interpenetrate with NBR molecular chains. Then the blends are cured at 120°C. During

Figure 9. Schematic diagram for the formation process of NBR/(PU-SiO₂) blends

the first 20 min of the curing process, the crosslinking reaction of PU-SiO₂ system plays a leading role. The NCO groups of PU prepolymer react with the OH groups of SiO₂ to form PU-SiO₂ hybrid networks. About 20 min later, the crosslinking reaction of NBR is dominant. The linear NBR molecular chains are crosslinked into three-dimensional networks under the action of vulcanization system. Therefore, the blends based on NBR and PU-SiO₂ hybrid materials are generated. The interpenetrating structures between NBR and PU-SiO₂ in the blends achieved in the blending process are preserved by the curing process, which is important for the excellent properties of the resulting NBR/(PU-SiO₂) blends.

3.2. Properties of PU-SiO₂ hybrid materials and NBR/(PU-SiO₂) blends

3.2.1. Curing characteristics

The vulcanization curves of NBR, PU-SiO₂ and NBR/(PU-SiO₂) compounds with different PU-SiO₂ loading are graphically represented in Figure 10. The vulcanization characteristics, expressed in terms of the vulcanization times, t_{s2} (scorch time) and t_{90}

Figure 10. Vulcanization curves of (a) neat NBR, (b) NBR/(PU-SiO₂)-10, (c) NBR/(PU-SiO₂)-20, (d) NBR/(PU-SiO₂)-30, (e) NBR/(PU-SiO₂)-40, (f) NBR/(PU-SiO₂)-50 and (g) PU-SiO₂

(optimum cure time), as well as the maximum and minimum values of the torque, S_{max} and S_{min} , respectively, and delta torque ΔS ($\Delta S = S_{max} - S_{min}$), are deduced from the curves. These parameters, along with the cure rate index, CRI , expressed as $CRI = \Delta S / (t_{90} - t_{s2})$, which indicates the rate of cure of the compounds, are compiled in Table 3. A higher value of CRI means a higher rate of vulcanization.

It was found that, compared with those of NBR and PU-SiO₂, the t_{s2} and t_{90} of NBR/(PU-SiO₂) compounds with different PU-SiO₂ loading are sharply reduced with the addition of PU-SiO₂. The NBR/(PU-SiO₂) compound with 50 wt% PU-SiO₂ has t_{s2} and t_{90} of 8.22 and 34.93 min, respectively, which show decreases of 84.3 and 62.1% compared with those of neat NBR. The cure rate index values of the NBR/(PU-SiO₂) compounds, show an increase with addition of PU-SiO₂ and exceed those of the NBR and PU-SiO₂. The decreases in the scorch time and cure time accompanied with the increase in CRI of NBR/(PU-SiO₂) compounds indicate that NBR system and PU-SiO₂ system tend to have an accelerating effect on the cure. These results are consistent with the conclusions derived from the reduced reaction peak times for the NBR system and PU-SiO₂ system in the NBR/(PU-SiO₂)-50 compound. The minimum torque shows a decrease with increasing PU-SiO₂ content for all NBR/(PU-SiO₂) compounds. This indicates that the processability of the compounds is improved after the incorporation of PU-SiO₂. The increasing maximum torque indicates higher modulus as a result of the PU-SiO₂ addition. This is further supported by the increase in the difference between the maximum and minimum torque, ΔS , upon PU-SiO₂ loading. As a consequence, PU-SiO₂ acts as a processing aid (improving the rheological properties of NBR) besides having an accelerating effect on the NBR vulcanization process. Note that, with increasing PU-SiO₂ content, especially when the PU-SiO₂ content achieves

Table 3. Vulcanization characteristics of NBR, PU-SiO₂ and NBR/(PU-SiO₂) compounds with different PU-SiO₂ loading

PU-SiO ₂ content [wt%]	t_{s2} [min]	t_{90} [min]	S_{min} [dNm]	S_{max} [dNm]	ΔS [dNm]	CRI [dNm/min]
0 (NBR)	52.37	92.23	2.2	18.6	16.4	0.41
10	30.25	53.93	1.9	17.4	15.5	0.65
20	23.63	40.55	1.8	17.7	15.9	0.94
30	15.35	36.48	1.5	18.1	16.6	0.79
40	8.58	34.52	1.2	20.3	19.1	0.74
50	8.22	34.93	1.1	22.4	21.3	0.80
100(PU-SiO ₂)	49.42	110.93	0.3	25.7	25.4	0.41

50 wt% (Figure 10f), the vulcanization curves of NBR/(PU-SiO₂) compounds appear to indicate two stages of cure acceleration. As can be seen from Figure 10f, one vulcanization accelerating stage begins at about 380 s, and the other begins at about 1490 s for the NBR/(PU-SiO₂)-50 compound. The former stage is attributed to the crosslinking of PU-SiO₂ and the latter to the crosslinking of NBR, which is consistent with the two exothermic peaks of NBR/(PU-SiO₂)-50 compound during the isothermal curing at 120°C. However, a possible mechanism for explaining this phenomenon is still under investigation.

3.2.2. Dynamic mechanical analysis

The DMA curves and data for the NBR, PU-SiO₂ and NBR/(PU-SiO₂) blends with different PU-SiO₂ loading are reported in Figure 11 and Table 4, respectively. From Figure 11 and Table 4, it can be seen that the $\tan\delta$ of the neat NBR exhibits one peak at -17.8°C , which corresponds to the T_g , whereas PU has a T_g around -23.6°C when we consider the position of the related $\tan\delta$ peaks. As for all the NBR/(PU-SiO₂) blends, the T_g around -20°C is assigned to NBR, however the glass transition of PU-SiO₂ is not obvious. With the increasing of PU-SiO₂ content in the blends, the T_g of NBR in the NBR/(PU-SiO₂) blends shifts to a lower temperature and locates between the T_g s of neat NBR and PU-SiO₂. The result indicates that the compatibility

between NBR phase and PU-SiO₂ phase is improved in the NBR/(PU-SiO₂) blends [25, 26]. From the above TEM analysis, we can see that with more PU-SiO₂ incorporated in NBR, the interpenetration and entanglement structures between NBR and PU-SiO₂ increase. The entanglement of the two polymers networks leads to forced ‘compatibility’ [27], which can not be achieved by usual blending method. As a result, the compatibility of NBR and PU-SiO₂ is improved with increasing PU-SiO₂ content. The broadening of the $\tan\delta$ peaks and decrease of T_g suggest that the damping properties and low temperature resistance of the blends are improved [28, 29]. With the addition of PU-SiO₂, a noticeable reduction in $\tan\delta$ peak height can be observed. The peak height of $\tan\delta$ curve decreases from 1.223 for NBR to 0.632 for NBR/(PU-SiO₂)-50 blend. The reduction in the $\tan\delta$ peak height can be correlated with the morphology of this blend. As discussed in TEM analysis, in NBR/(PU-SiO₂)-50 blend, the NBR and PU form a co-continuous morphology, which enhances interpenetration and entanglement of the two phases and restricts the motion of the polymers molecular chains. As a result, the $\tan\delta$ peak height reduces greatly.

From the DMA curves of the storage modulus (E') versus temperature, it is evident that the more PU-SiO₂ is incorporated in the NBR, the higher the modulus in the rubbery plateau of the NBR is, which shows that the addition of PU-SiO₂ into NBR results in a remarkable increase of stiffness. This observation provides further evidence that the strong confinement of interpenetration network on the rubber chains. These results are in accordance with that the $S_{\max}$ increases with adding PU-SiO₂.

3.2.3. Mechanical properties

The stress-strain behaviors of NBR, PU-SiO₂ and NBR/(PU-SiO₂) blends with different PU-SiO₂ loading are presented in Figure 12 and Table 5. From the results it can be seen that NBR shows very poor mechanical properties. It is quite obvious because of the fact that NBR is a random copolymer having no regular structure. However, with the incorporation of the PU-SiO₂ in the NBR matrix, significant

Figure 11. Storage modulus and $\tan\delta$ versus the temperature for NBR, PU-SiO₂ and NBR/(PU-SiO₂) blends with different PU-SiO₂ loading

Table 4. DMA data of NBR, PU-SiO₂ and NBR/(PU-SiO₂) blends with different PU-SiO₂ loading

PU-SiO ₂ content [wt%]	0 (NBR)	10	20	30	40	50	100 (PU-SiO ₂)
T_g [$^\circ\text{C}$]	-17.8	-18.5	-18.9	-19.2	-21.1	-22.3	-23.6
$\tan\delta_{[\max]}$	1.22	1.17	1.06	0.91	0.75	0.63	0.3

Table 5. The data of stress-strain behaviors of NBR, PU-SiO₂ and NBR/(PU-SiO₂) blends with different PU-SiO₂ loading

Properties	PU-SiO ₂ content [wt%]						
	0 (NBR)	10	20	30	40	50	100 (PU-SiO ₂)
100% Modulus [MPa]	1.3±0.1	1.5±0.1	1.7±0.1	2.1±0.1	2.8±0.1	3.5±0.1	5.6±0.1
300% Modulus [MPa]	–	3.0±0.1	3.6±0.2	4.6±0.1	6.1±0.1	8.1±0.1	13.1±0.2
Tensile strength [MPa]	1.9±0.4	8.0±0.5	14.0±0.5	20.6±0.6	23.5±0.5	25.2±0.5	26.0±0.5
Elongation at break [%]	281±10	481±13	520±12	535±15	518±12	530±12	406±13
Tear strength [kN/m]	8.2±1.0	20.8±1.2	25.8±1.3	31.7±0.9	40.2±1.1	52.3±0.9	58.4±1.0
Shore A hardness	52	53	55	63	65	72	81

increases in the modulus, tensile strength, elongation at break, hardness and tear strength are achieved (Table 5). When the PU-SiO₂ content increases from 0 to 50 wt%, the tensile strength and tear strength increase from 1.9 MPa and 8.2 kN/m to 25.2 MPa and 52.3 kN/m, which are 1226 and 538% higher than those for NBR respectively. This demonstrates that the PU-SiO₂ hybrid network could significantly enhance the NBR vulcanizate. This is consistent with the above morphology results. The formation of quasi-IPN structures in the blends with

high PU-SiO₂ content are beneficial to the improvement of the mechanical properties [30, 31], as the mechanical properties of the systems reach maximum for the NBR/(PU-SiO₂) blends. The tensile strength and tear strength as a function of weight fraction of PU-SiO₂ in blends are shown in Figure 13. As can be seen, the tensile strength and tear strength of the NBR/(PU-SiO₂) blends show a positive deviation from linearity in all cases, which exhibits synergistic behavior. The improved mechanical properties and synergistic behavior are mainly caused by the good compatibility of NBR and PU-SiO₂ [32]. The elongation at break of the NBR/(PU-SiO₂) blends increases with the addition of PU-SiO₂ and exceeds those of the neat NBR and PU-SiO₂, which exhibits that the incorporation of PU-SiO₂ hybrid network does not deteriorate the elasticity of the NBR.

Figure 12. The stress-strain behaviors of NBR, PU-SiO₂ and NBR/(PU-SiO₂) blends with different PU-SiO₂ loading **Figure 13.** Dependence of tensile strength and tear strength of NBR/(PU-SiO₂) blends on the PU-SiO₂ content **Figure 14.** Effect of the amount of PU-SiO₂ on the Akron abrasion loss and flex-fatigue life of NBR/(PU-SiO₂) blends

50 wt%, the value of Akron abrasion loss decreases from 2.71 to 0.71 cm³/1.61 km, which is 73.8% lower than that for NBR. It can be seen that the PU-SiO₂ hybrid network can enhance the abrasion resistance of NBR greatly. It is well known that the abrasion resistance of PU is excellent [33]. The PU crosslinked by SiO₂ preserves the outstanding abrasion resistance, the Akron abrasion loss of which is 0.45 cm³/1.61 km. The abrasion resistance improvement of NBR after incorporation of PU-SiO₂ is mostly because of the excellent abrasion resistance of the PU-SiO₂.

From the curves of flex-fatigue life versus PU-SiO₂ content, it can be seen that when the PU-SiO₂ content is less than 20 wt%, the flex-fatigue life improvement is not great, while as the PU-SiO₂ content exceeds 20 wt%, the flex-fatigue life is dramatically improved. Especially when the PU-SiO₂ amount increased from 20 to 30 wt%, increasing the PU-SiO₂ amount by only 10 wt% causes that the flex-fatigue life to increase nearly 10 times, from 7.2 thousand cycles to 70 thousand cycles. It is important to point out that the flex-fatigue life of neat NBR and PU-SiO₂ hybrid materials are 2.5 and 3.5 thousand cycles, respectively. However, the flex-fatigue life of NBR/(PU-SiO₂)-50 blend is 280 thousand cycles, which is more than 100 times that of neat NBR. It can be seen the flex-fatigue life of the individual components are relatively poor, while the flex-fatigue life of the resulting NBR/(PU-SiO₂) blends are improved significantly. The great improvement of flex-fatigue life of the NBR/(PU-SiO₂) blends may be explained in terms of the microstructures suggested in TEM analysis. With the increasing of PU-SiO₂ content, the interpenetration and entanglement structures between NBR and PU-SiO₂ increase, these structures are beneficial to the improvement of flex-fatigue life.

4. Conclusions

Novel blends of NBR and in-situ produced PU-SiO₂ hybrid networks were prepared successfully by melt blending. The PU-SiO₂ hybrid networks were formed via the reaction of NCO groups of PU prepolymer and OH groups of SiO₂ in the absence of an external crosslinking agent (i.e. alcohols and amines) during the curing process of NBR. The incorporation of PU-SiO₂ into NBR matrix led to

higher curing rate, this is due to the mutual cure accelerating effects of NBR system and PU-SiO₂ system. Transmission electronic microscopy (TEM) studies indicated that the interpenetration and entanglement structures between NBR and PU-SiO₂ increased with increasing PU-SiO₂ content and the quasi-interpenetrating polymer networks (quasi-IPN) structures were formed when the weight content of PU-SiO₂ was 50% in the NBR/(PU-SiO₂) systems. The DMA results showed that the compatibility between NBR and PU-SiO₂ was improved with PU-SiO₂ loading. The PU-SiO₂ hybrid network showed promising reinforceability towards the NBR compounds. The modulus, tensile strength, tear strength and hardness were found to be increased consistently with the content of PU-SiO₂. When the PU-SiO₂ content was 50 wt%, 1226 and 538% increases of tensile strength and tear strength of the neat NBR vulcanizate were achieved. The abrasion resistance and flex-fatigue life of NBR were improved significantly by the incorporation of PU-SiO₂. Further work will focus on the studies of reaction kinetics and phase separation kinetics of NBR and PU-SiO₂ components in the NBR/(PU-SiO₂) blends, and the factors affecting the reaction and phase separation kinetics. The purposes of these studies are to get finer structures in the NBR/(PU-SiO₂) blends, which is important for the performance improvement of the blends.

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