Green Thermoplastic Vulcanizates Based on Silicone Rubber and Poly(butylene succinate) via In Situ Interfacial Compatibilization

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ABSTRACT: Presenting a combination of sustainability and environmental friendliness, a new class of green and non-petroleum-based thermoplastic vulcanizates (TPVs) was successfully developed from silica-filled silicone rubber (FSR) and poly(butylene succinate) (PBS) via dynamic vulcanization. The phase morphology, interfacial compatibilization, and microstructural properties of FSR/PBS TPVs were investigated. Notably, a large number of FSR microparticles were observed and dispersed in the continuous PBS phase, indicating complete phase inversion during the dynamic vulcanization. The fine phase morphology of FSR/PBS TPVs was achieved by a fine phase morphology of the SR/PBS premix, the good interfacial compatibility between the PBS phase and the cross-linked FSR phase, and complete phase inversion. The as-prepared TPVs possessed high tensile strength, good elastic behavior, easy processability, and reprocessability. These novel non-petroleum-based TPVs have potential applications in packagings, biomedical devices, and three-dimensional (3D) printing materials.

INTRODUCTION

Thermoplastic elastomers (TPEs) are a promising class of materials that combine the elasticity of traditional vulcanized rubber with the processability of thermoplastics.1−3 Dynamic vulcanization (DV) of polymer blends is an effective and economical method to fabricate TPEs based on rubber and thermoplastics, i.e., a great amount of cross-linked rubber particles dispersed in a small amount of thermoplastic.4−6 Compared with thermoplastic block copolymers, the physical properties of a thermoplastic vulcanizate (TPV) are closer to those of traditional thermoset rubbers, which have excellent elastic properties and mechanical properties. Recently, TPVs have become the fastest-growing elastomers, replacing unrecoverable thermoset rubbers because of environmental protection and resource conservation requirements. Thus, TPVs are widely used as “green” elastomers in automotive, construction, electronic cable, and other industries.6−10 Particularly, critical roles in the properties of TPVs are played by the content and cross-linking degree of the rubber phase, the size and size distribution of the rubber phase and corresponding rubber network structure, the thickness of the plastic ligaments and the compatibility between plastic and rubber. To obtain high-elasticity TPVs, a high (60–80 wt %) rubber phase content is necessary, resulting in a continuous rubber phase in the premix before DV. Moreover, to achieve good processability and easy recyclability, a continuous plastic phase is required. Therefore, the key to preparing TPVs is the realization of the phase inversion of the rubber phase from a continuous phase (in the premix) to a dispersed phase (in the TPV).3,11 Furthermore, a fine dispersed rubber phase facilitates good mechanical properties in the final TPV. Although the highly cross-linked rubber phases disperse in the system, TPVs also exhibit elasticity as good as that of traditional cross-linked rubber.

Various types of high-performance TPVs composed of different rubbers and thermoplastics have been explored using DV techniques. The rubber components include ethylene propylene diene rubber (EPDM), nitrile butadiene rubber, isobutylene-isoprene rubber, natural rubber (NR), epoxidized natural rubber (ENR), silicone rubber, acrylic rubber, and ethylene-vinyl acetate rubber. Meanwhile, the thermoplastics explored include polypropylene (PP), high-density polyethylene, polyamide (PA), and polyurethane.2−25 EPDM/PP TPVs4,26 are currently the first commercial TPV products, mainly because the good compatibility between EPDM and PP results in finely dispersed rubber particles without any compatibilizer.

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Presently, because of the fossil fuel limitations, environmental concerns, and climate change, non-petroleum-based TPVs are attracting increasing attention and providing sustainable alternatives to petroleum-based TPVs. Previous investigations of non-petroleum-based TPVs have mainly focused on the blending of polyactide (PLA) with NR, ENR, or bio-based polyester elastomers via DV. Chen and coauthors prepared PLA/NR TPVs and PLA/ENR TPVs, which emphasized the improvement of PLA toughness and shape memory behaviors. Kang and Hu et al. fabricated fully bio-based TPVs using PLA and synthesized bio-based polyester elastomers (synthesizing from sebacic acid, itaconic acid, succinic acid, 1,3-propanediol, lactic acid, or 1,4-butanediol). They found that a large amount of bio-based polyester elastomers was dynamically vulcanized and dispersed in a continuous PLA phase, showing that the phase inversion was realized. More broadly, it remains a pressing need to develop suitable TPVs to meet sustainable development requirements and conserve petroleum resources.

Silicone rubber (SR), which is derived from silicates in the earth’s crust, is an important kind of non-petroleum-based synthetic rubber. Recently, some SR-based TPVs have been designed and fabricated for special purposes, thanks to their excellent temperature and aging resistance, thermal stability, and dielectric properties. However, the current SR-based TPVs were concentrated on mixing with petroleum-based plastics, such as poly(vinylidene fluoride), PA12, PP, and thermoplastic polyurethane. Thus, adopting bio-based plastic to fabricate TPV can provide a sustainable alternative for these petroleum-based TPVs.

In this study, a blend of SR with poly(butylene succinate) (PBS) was chosen to develop a new non-petroleum-based TPV using the DV technique. Based on its thermal and chemical resistance temperatures, biodegradability, processability, and biocompatibility, PBS as an eco-friendly, renewable polymer has attracted wide research attention. Our design addresses the disparity may favor phase inversion. Subsequent investigation adopted FSR and PBS as the rubber and plastic components, respectively.

**RESULTS AND DISCUSSION**

**Dynamic Vulcanization of FSR/PBS TPVs.** *Viscosity.*

The viscosity of the rubber phase has the potential to affect not only the phase morphology of the premix but also the breakup of its domains during DV, thereby influencing the TPV microstructure, especially the final size and distribution of the rubber particles. The shear viscosity as a function for shear rate for SR, PBS, and FSR at 120 °C is provided in Figure 1. The trends in the shear viscosity curves suggest that all samples show shear-thinning behavior. As shown in Figure 1, the viscosity of SR is much lower than that of PBS. In the preparation of the SR/PBS premix, the SR phase, with its relatively lower viscosity, cannot provide sufficient shear stress to break up the PBS phase; this inability results in extremely distinct phase separation and prevents phase inversion. A digital photograph of SR/PBS TPV is shown in Figure S1. The cross-linked SR broke into powders, leaving PBS in the form of blocks. Therefore, we compounded the SR with silica to increase the viscosity of the SR phase. Previous studies have shown that a higher rubber/plastic viscosity ratio leads to the formation of a fine phase morphology, by making the coalescence and agglomeration of the rubber domains more difficult in TPVs. The viscosity of SR with silica (FSR) is much higher than that of PBS over a wide range of shear rates; this disparity may favor phase inversion. Subsequent investigation adopted FSR and PBS as the rubber and plastic components, respectively.

**DV Process.** The mixing torque and temperature with time during DV of the FSR/PBS premix are presented in Figure 2.

The mixing torque first increased with mixing time because of the increasing shear rate and subsequently increased due to the rapid cross-linking of the FSR phase. After reaching its maximum value, the torque slowly declined and reached a plateau with the completion of phase inversion. The temperature curve showed a continuous decrease with the introduction of the cold FSR/PBS premix into the hot mixer and the melting of the blends. Then, the temperature increased continuously, surpassing the set temperature due to cross-
linking and shearing friction. The torque and temperature curves are similar to those of other TPVs. In Situ Interfacial Compatibilization of FSR/PBS TPVs.

If the rubber and plastics were incompatible, the fabricated TPVs would exhibit a coarse phase morphology, a poor interfacial interaction between the rubber and plastic, and thus poor properties. In such cases, it would be necessary to compatibilize the rubber and plastic to obtain a fine phase morphology and a good interfacial interaction for good properties. Scanning electron microscopy (SEM) images of cryo-fractured surfaces for FSR/PBS TPVs are presented in Figure 3. The figure shows no obvious voids on the fractured surfaces of FSR/PBS TPVs. In addition, the phase interface in FSR/PBS TPVs could not be clearly distinguished in the SEM images. These results possibly indicate some compatibility and a strong interfacial interaction between the FSR and PBS phases in TPVs.

To evaluate interfacial compatibilization during DCP-induced DV, Fourier transform infrared (FTIR) analysis was used to investigate the possible reaction between PBS and FSR. FSR/PBS TPVs were extracted by dichloromethane (DCM) after 72 h; the free PBS was removed completely from FSR/PBS TPVs, and some insoluble residues were obtained. The FTIR spectra of PBS, FSR, and the FSR/PBS TPV insoluble residues are shown in Figure 4. According to FTIR curves, PBS shows the stretching vibration absorption of $\text{C=O}$ at 1722 cm$^{-1}$ and the stretching vibration absorption of $\text{C-O}$ at 1159 cm$^{-1}$; these belong to the characteristic of ester groups. The characteristic FSR peaks at 1077 and 1013 cm$^{-1}$ are the stretching vibration absorptions of $\text{Si-O}$, whereas the peak at 795 cm$^{-1}$ is the stretching vibration absorption of $\text{Si-CH}_3$, and the peak at 1259 cm$^{-1}$ are specific to the stretching vibration absorption of $\text{CH}_3$. The insoluble residues of FSR/PBS TPVs showed spectra similar to those of FSR, indicating that the free PBS was completely extracted by DCM after 72 h. Notably, the characteristic absorption of $\text{C=O}$ at ~1725 cm$^{-1}$ was observed in the FTIR spectra of the residues, suggesting that the PBS polymer chains might be chemically bonded to FSR.

Figure 3. SEM images of FSR/PBS TPVs: (a) FSR/PBS-50, (b) FSR/PBS-60, (c) FSR/PBS-70, and (d) FSR/PBS-80.

Figure 4. (a) FTIR spectra of PBS, FSR, and the FSR/PBS TPV insoluble residues. (b) FTIR absorbance area changes in $A_{\text{C=O}}/A_{\text{Si-CH}_3}$ of residues for FSR/PBS TPVs.
polymer chains during DCP-induced DV. The preparation of FSR/PBS TPVs and a plausible reaction between PBS and SR phases are depicted in Scheme 1. According to relevant studies, PBS radicals are generated by DCP’s abstraction of hydrogen atoms from polymer chains.44 PBS radicals may react with FSR radicals at the interfaces of PBS and SR phases, forming chemical bonds.

To obtain the detailed information about the interface reaction, the relative proportion of PBS in the insoluble residues was calculated using the ratio of the intensities of two FTIR absorbances: C=O of PBS and Si–CH$_3$ of FSR. The percentage change in $A_{\text{C}=\text{O}}/A_{\text{Si–CH}_3}$ is shown in Figure 4b. The curve demonstrates that the percentage change in $A_{\text{C}=\text{O}}/A_{\text{Si–CH}_3}$ increases with the increase of the FSR content. Because the dosage of DCP was calculated using that of rubber, the actual dosage of DCP increased with the increase of the FSR content. Higher dosage DCP would generate more macromolecular radicals of PBS and SR, resulting in the formation of more grafting copolymers at the interfaces.

In addition, the gel content of FSR/PBS TPVs is shown in Figure 5, which was determined by extraction in DCM for 72 h, and the free PBS was removed completely from FSR/PBS TPVs. The FSR gel content increases with the increase of the FSR content. For FSR/PBS-80, the value of the gel content actually reaches beyond 100%. As the dosage of DCP relative to FSR is identical in all of the samples, such an increase in the gel content is related to some additional chemical points forming between PBS and SR macromolecular chains. This result is consistent with the FTIR results.

**Phase Morphology of FSR/PBS TPVs.** The TPV morphology, which is one of the most crucial characteristics, results from complex interrelationships among processing conditions, cross-linking reaction, composition, viscosity and elasticity ratios of individual components, and so on. Among the various moduli considered for the PBS and FSR phases, PF-AFM was used to study the phase morphology of FSR/PBS TPVs; modulus images are shown in Figures 6 and 7. In these figures, the lighter regions with a higher modulus represent the PBS phase and the darker regions with a lower modulus represent the FSR phase. As Figure 6a shows for FSR/PBS-70 before DV, the PBS phase is dispersed in a continuous FSR phase because of the high proportion of the FSR phase. In contrast, FSR/PBS-70 after DV (Figure 6b) exhibits a vast cross-linked FSR phase dispersed in a continuous PBS phase, indicating the occurrence of phase inversion. As the DV proceeded, the continuous FSR phase broke into microparticles and transformed into a dispersed phase in the continuous PBS phase because of the rapid increase in viscosity and the resulting shear stress acting on the FSR phase.

The phase morphology of FSR/PBS TPVs with various FSR contents is shown in Figure 7. As expected, the cross-linked
FSR particles were dispersed in a continuous PBS phase and a typical sea-island structure was formed within TPVs, indicating that the phase inversion occurred during DV. A relatively fine morphology of FSR/PBS TPVs was obtained with the diameters of 0.5–3.0 μm for cross-linked FSR particles. This is probably due to three reasons: (i) the matching viscosity of FSR to that of PBS, which benefits the breakup of the PBS phase and the formation of smaller particles in the FSR/PBS premix; (ii) the good interfacial compatibility between the PBS phase and the cross-linked FSR phase, as some PBS polymer chains were chemically bonded to FSR polymer chains at the interface of the two phases during the DV process; and (iii) the complete phase inversion, which results in a great amount of cross-linked FSR particles uniformly dispersed in the PBS matrix. In addition, an FSR phase in FSR/PBS-80 showed an apparent aggregation tendency and exhibited stretched and elongated structures. This phenomenon is mainly due to the fact that higher the FSR content results in greater difficulty in the breakup of cross-linked FSR particles and in phase inversion. Therefore, these results suggest that the blending ratio of rubber to plastic greatly influences the phase morphology of TPVs. Besides, disintegration tests were adopted to confirm the phase morphology. The photographs of the FSR/PBS TPVs immersed in DCM are provided in Figures S2 and S3. All of the TPV samples completely disintegrated into small pieces after 20 min, exhibiting the typical sea-island structure and indicating the completion of phase inversion.

A rubber process analyzer (RPA) test was then used to further investigate the rubber networks in FSR/PBS TPVs. The variation in storage modulus (G’) with strain for FSR/PBS TPVs is shown in Figure 8. It can be seen that G’ gradually decreased with the increase of total strain; this phenomenon is similar to the so-called Payne effect of filled rubber systems. The cross-linked FSR particles can be considered as the fillers dispersed in the PBS matrix. With increasing strain, the cross-linked FSR networks disintegrated, resulting in a decline in G’. Larger ranges of G’ values indicate the stronger rubber networks in TPV and a stronger Payne effect. In Figure 8, G’ clearly increased with the increase of the FSR content, suggesting that a higher FSR content produced a stronger network in TPV. For FSR/PBS-80, the relatively high value for G’ was due to the increase in the number of elastic cross-linked features and agglomerates of cross-linked FSR particles. The agglomerates of cross-linked FSR particles were consistent with the AFM results.

Properties of FSR/PBS TPVs. TPV properties were significantly affected by the phase morphology, especially the size of the dispersed rubber phase, rubber network structure, and thickness of the plastic ligaments. FSR/PBS TPV properties, including the rheological, elastic, and mechanical properties, and reprocessability were investigated; the results are shown in Figures 9–12.

Rheological Properties. The rheological properties of TPVs, dominated by the continuous plastic matrix, acted as a pivotal part in the melt processability, recyclability, and production efficiency of TPVs. Capillary rheometry was applied to determine the rheological behavior of FSR/PBS TPVs; the results are shown in Figure 9. FSR/PBS TPV viscosity significantly decreased with the increase of the shear rate; this behavior indicates the pseudoplastic flow behavior of TPVs. The viscosities of the TPVs were much greater than those of PBS, especially at low shear rates; this result indicates the formation of a strong interface interaction between the PBS and FSR phases. Typically, the microstructure of the polymer determines the rheological properties. The cross-linked rubber particles were not easily deformed and retained their
morphology in the melt even at high shear rates, leading to TPV viscosities being higher than those of PBS, while under high shear rates, the breakdown of the rubber networks formed by FSR particles caused a clear decrease in viscosity. Furthermore, the viscosity of FSR/PBS TPVs increased with the increase of the FSR content. This finding is mainly attributed to a stronger rubber network caused by an increase in the number and numerical density of rubber particles in TPVs. Notably, the viscosities of FSR/PBS TPVs are below 10^3 Pa·s under high shear rates, indicating good processibility of these TPVs.

Elasticity. TPV elasticity was supplied by the high content and high cross-linking degree of the rubber phase. Hysteresis loss and permanent set are widely used as indicators of the elastomer elasticity. Tensile recovery tests were performed on FSR/PBS TPVs to investigate elasticity. FSR/PBS TPVs were stretched to a strain of 50% and then allowed to recover, as shown in Figure 10. The hysteresis losses and the permanent deformations of TPVs were higher than those of traditionally vulcanized rubbers. With the increase of the FSR content, the permanent deformations and hysteresis losses of FSR/PBS TPVs decreased. This finding was ascribed to the higher FSR content and the stronger rubber network, which provided a sufficient recovery force from a highly deformed state.

Mechanical Properties. The stress–strain curves of FSR/PBS TPVs as functions of FSR content are shown in Figure 11. As shown in Figure S4, PBS showed characteristic features of a tough material, such as relatively high tensile strength and elongation at break. In contrast, FSR presented typical elastomeric characteristics, such as low tensile strength and high elongation at break. All of the FSR/PBS TPV stress–strain curves exhibited elastic behavior: soft and tough. With the increase of the FSR content, the tensile strength and elongation at break of FSR/PBS TPVs decreased. In addition, FSR/PBS-80 exhibited inferior tensile strength and elongation at break, due to the increased number of agglomerates of cross-linked FSR, as shown in Figure 7d. On the basis of the above results, FSR/PBS-70 seems to be an optimal composition with high tensile properties and good elastic behavior, inasmuch as a further increase in the FSR content would deteriorate TPV mechanical properties. For FSR/PBS-70, a tensile strength of 10.8 MPa and an elongation at break of 424% could meet performance requirements for use as general elastomers. The satisfying mechanical properties are ascribed to the strong interfacial adhesion between the PBS and FSR phases, which facilitates the inner stress transfer from the rigid plastic phase to the soft rubber phase, thus preventing the growth to the catastrophic failure of the cracks initiated at the phase interface. In addition, SiO₂ effectively stiffens and strengthens SR.

Reprocessability. Reprocessability is one of the major advantages of the TPVs because of the requirements of environmental protection and resource saving. As examples, the reprocessability of FSR/PBS-70 was studied and the change in the tensile stress and the elongation at break are shown in Figure 12. It can be seen that both the tensile stress and the elongation at break of FSR/PBS-70 slightly decreased with reprocessed three times, owing to the thermal degradation of PBS undergoing long high-temperature processing. After reprocessed three times, the tensile stress and the elongation at break decreased by 24 and 19%, respectively. This proved that FSR/PBS TPVs showed relatively good reprocessability without a significant decrease in the mechanical properties.

CONCLUSIONS

We transcended compatibility and viscosity-matching obstacles to successfully fabricate a desired thermoplastic vulcanizate (TPV) from silica-filled silicone rubber and poly(butylene succinate) via dynamic vulcanization (DV). The as-prepared TPVs possessed good mechanical properties, good elasticity, and easy processability. More importantly, in situ interfacial compatibilization between the FSR and PBS phases was induced by dicumyl peroxide. This compatibilization was
confirmed by the observation of characteristic PBS absorptions in the FTIR spectra for the insoluble residues of TPVs, as well as by the increased gel content of TPVs. The AFM images, disintegration tests, and RPA results demonstrated that FSR/PBS TPVs exhibited the typical sea-island structure with vast, well-dispersed cross-linked FSR particles in a continuous PBS phase, indicating the completion of phase inversion during DV. Moreover, the tensile strength and elongation at break of TPVs ranged, respectively, from 5.1 to 11.8 MPa and from 152 to 534%; hysteresis losses and permanent deformations decreased with the increase of the FSR content, implying an increase in TPV elasticity. In addition, all FSR/PBS TPVs showed easy processability and reprocessability, which is very highly convenient for industrial applications.

■ EXPERIMENTAL SECTION

Materials. Methyl vinyl silicone rubber (SR, 110-2, vinyl contents: 0.13–0.20%) was purchased from Dongjue Silicone Group Co., Ltd., China. Silica and hydroxyl-terminated dimethyl siloxane (HDMS) were provided by Shenyang Yixiang Material Co., Ltd., China. Poly(butylene succinate) (PBS) was supplied by China Kingfa Sci. & Tech. Co., Ltd., China. Dicumyl peroxide (DCP) and antioxidant pentaerythritol tetrakis 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (1010) were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

Preparation of FSR/PBS TPVs. Preparation of FSR. In total, 60 wt % of SR, 35 wt % of silica, and 5% of HDMS were premixed in an internal mixer (RM-200A, Harbin Hapro Electric Technology Co., Ltd., China) at 40 °C. Silica was used to improve the viscosity of SR, whereas HDMS was used to improve the dispersion of silica in SR. The obtained compounds are heretofore referred to as FSR, and the morphology of FSR is shown in Figure S5.

Preparation of FSR/PBS TPVs. The dynamically cross-linked FSR/PBS premix was prepared by the following steps. The FSR, PBS, antioxidant, and DCP were melt-mixed in an internal mixer at 120 °C for 10 min to produce FSR/PBS premixes with various rubber/plastic weight ratios (50/50, 60/40, 70/30, and 80/20). Then, each FSR/PBS premix was dynamically cross-linked at 170 °C for 8 min at a rotational speed of 80 rpm in an internal mixer. Subsequently, each cross-linked sample was hot-pressed at 120 °C to obtain a sheet of 1 mm thickness. For brevity, the TPV containing 60 wt % FSR is abbreviated as FSR/PBS-60.

Characterization. Morphological characterization was performed using an SU8010 scanning electron microscope (SEM; Hitachi Co., Ltd., Japan). The sample fractured in liquid nitrogen was surface-coated with a thin gold layer. The morphology was also observed using the PeakForce QNM mode on a Bruker MultiMode atomic force microscope (AFM) at ambient conditions. The observed sample was polished at −130 °C using a cryo-ultramicrotome (Leica EM UC7, Germany).

Extractions using dichloromethane (DCM) were used to determine the gel content of the FSR phase. Approximately 1 g of TPV was weighed \( (M_0) \) and placed in an 80-mesh copper pouch. The pouch was also weighed \( (M_f) \) and then extracted with a Soxhlet extraction apparatus in DCM at 40 °C for 72 h to selectively etch the free PBS component. The weight of the pouch \( (M_g) \) was determined after the sample was dried in a vacuum oven at 50 °C for 24 h. The FSR gel content was calculated as

\[
gel = \frac{M_0 - M_g}{M_0} \times 100\n\]

where \( W_{FSR} \) is the FSR mass fraction.

Fourier transform infrared (FTIR) spectroscopic analysis was performed using a Nicolet10 Fourier transform spectrometer. The measurement resolution was set at 4 cm\(^{-1}\), and the spectra were collected in the wavenumber range of 400–4000 cm\(^{-1}\). The test sample is insoluble matter extracted by DCM.

TPV rubber network measurements were performed using a rubber process analyzer (RPA-8000, Gotech Testing Machines Co., Ltd., China). The strain sweep was from 0.2 to 470% at 170 °C and 0.2 Hz. The sample was preheated at 170 °C for 5 min.

The tensile tests were carried out using an INSTRON 3365 testing machine (Instron Co., Ltd.) according to ASTM D412 with a crosshead speed of 200 mm/min at 25 °C. At least five specimens were tested to obtain each average value.

In strain recovery tests, the strain was extended to 50%, and then the tensile force was set to zero; the residual strain was defined as the permanent set. The hysteresis loss (HL) at 50% elongation was calculated as

\[
HL = \frac{F_1 - F_2}{F_2} \times 100
\]

where \( F_1 \) is the area under the stress–strain curve and \( F_2 \) is the area under the force–retraction curve.

The rheological properties of the samples were investigated using a capillary rheometer (Model RH 2000, Malvern Instruments Ltd., U.K.) at the given temperature under the single-bore experiment mode and a shear rate ranging from 20 to 1000 s\(^{-1}\). The \( L/D \) ratio of the capillary was 16/1. Each flow curve was generated from data collected at eight different shear rates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c06036.

Digital photograph of SR/PBS TPV (Figure S1); digital photographs of FSR/PBS TPVs immersed in DCM
(Figures S2 and S3); the stress–strain curves of PBS and FSR (Figure S4); and microscopy images of FSR (Figure S5) (PDF)

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Notes
The authors declare no competing financial interest.

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