

Static Flocculation in Carbon Black-filled Rubber: From Constrained Filler Motion to Polymer-driven Interfacial Reinforcement

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Electronic Supplementary Information

Abstract The flocculation behavior of carbon black (CB)-filled isoprene rubber (IR) nanocomposites was systematically investigated under both dynamic and static conditions to unravel the distinct mechanisms governing filler network evolution. Under dynamic conditions, small oscillatory shear strains (0.1%) significantly enhanced filler particle motion, leading to pronounced agglomeration and a flocculation degree of about 4.3 MPa at 145 °C. In contrast, static flocculation exhibited a fundamentally different mechanism dominated by polymer chain dynamics, which is driven mainly by thermal activation. Radial distribution function (RDF) analysis of transmission electron microscopy (TEM) images revealed a slight decrease (2 nm) in the interparticle distance peak after static annealing at 100 °C for 7 h, indicating localized motion of CB particles. However, the overall filler network remained stable, with no significant agglomeration observed. The increase in bound rubber content from about 23% to 28% with rising temperature further confirmed the dominant role of polymer chain adsorption and interfacial reinforcement in static flocculation. These findings highlight the critical influence of external strain on filler network formation and provide new insights into the polymer-dominated mechanism of static flocculation. The results offer practical guidance for optimizing the storage and processing of rubber nanocomposites, particularly in applications where static flocculation during prolonged storage is a concern.

Keywords Rubber compounds; Carbon black; Static flocculation; Particle motion; Bound rubber

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INTRODUCTION

Rubber nanocomposites are widely used in various industrial fields owing to their excellent mechanical properties,^[1] such as high elasticity,^[2] wear resistance,^[3,4] and fatigue life.^[5,6] The performance of these materials is significantly influenced by the dispersion of the filler within the rubber matrix.^[7] Extensive research has demonstrated that the improved dispersion of fillers can significantly enhance the mechanical properties of rubber nanocomposites, including tensile strength, fatigue resistance, and dynamic modulus.^[8–13] However, achieving and maintaining optimal filler dispersion remains a challenge, particularly during subsequent processing stages, such as storage, extrusion, or vulcanization.^[14–16] During these stages, thermal motion often induces re-agglomeration or rearrangement of the fillers and polymers, a phenomenon known as flocculation.^[17] This flocculation process can substantially alter the properties of

a material, particularly its dynamic modulus and electrical conductivity, making it a critical factor in rubber processing and performance.

Flocculation in filled rubber systems is generally attributed to the motion of filler particles, which leads to the formation of agglomerates and the evolution of filler network structures.^[18–22] This process is closely related to the Payne effect, a well-known phenomenon in rubber science where the storage modulus decreases with increasing strain amplitude, reflecting the breakdown of filler agglomerates or networks.^[23–26] The Payne effect becomes more pronounced after flocculation, further supporting the idea that filler aggregation and particle networking occur during this process.^[27–29] The magnitude of the Payne effect, quantified as the difference in the storage modulus between low and high strain amplitudes, is widely used as an indicator of the degree of flocculation.^[30] Studies have also identified correlations between flocculation degree and various parameters, such as annealing temperature, particle size, and polymer viscosity, which align with the particle diffusion coefficients predicted by the Stokes-Einstein (SE) equation.^[17,31] These findings indicate that particle diffusion plays a critical role in floc-

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culation dynamics.

To investigate flocculation, a rheological time sweep is commonly employed, which allows real-time monitoring of modulus changes. However, the influence of small strain amplitudes on flocculation remains poorly characterized. Beyond rheological approaches, electrical conductivity measurements have also been used to track flocculation processes, as changes in the aggregate structure of CB can alter the conduction pathways.^[32–34] For instance, Gerspacher *et al.* reported that conductivity increases during flocculation, suggesting the structural reorganization of CB aggregates.^[17] Additionally, computational simulations have provided valuable insights into the filler dynamics during flocculation. For example, Stöckelhuber *et al.* demonstrated that the flocculation degree increases with larger differences in the work of adhesion between fillers and polymers, replacing the thermal energy with interfacial adhesion in their model.^[22]

Despite these advancements, alternative theories propose that flocculation may not result solely from the motion of filler particles. Instead, it could primarily arise from enhanced polymer chain adsorption on carbon black surfaces, leading to an increased bound rubber content.^[35–39] Bound rubber is often referred to the portion of rubber chains strongly adsorbed on the filler surface, reflecting the strength of the filler-polymer interactions. Schwartz *et al.* observed that conductivity increased during flocculation, even though transmission electron microscopy (TEM) analysis showed no measurable changes in aggregate size or location. They proposed that bridged polymer chains between filler aggregates might enhance the conductivity, suggesting that polymer dynamics play a significant role in flocculation.^[40] Recent studies by Robertson *et al.* further supported this view by observing similar TEM images of compounds before and after annealing, although the Payne effect of the annealed compound exhibited a large increase compared to the as-mixed sample.^[41] This suggests that flocculation may involve complex interplay between filler aggregation and polymer chain dynamics, particularly through the formation and evolution of bound rubber.

However, significant gaps remain in our understanding of the flocculation mechanisms. Current research predominantly relies on indirect methods, such as conductivity measurements or the Payne effect analysis, to infer filler aggregation. Direct observations of filler behavior during flocculation remain limited. Furthermore, while bound rubber content has been extensively studied, the evolution of its distinct components, that is, the glassy, secondary, and loose layers, during flocculation remains poorly characterized. Additionally, static flocculation occurring during industrial storage in the absence of applied strain has received considerably less attention than dynamic flocculation, which often occurs under oscillatory shear forces. This lack of understanding hinders the optimization of rubber processing techniques and prediction of material performance under different conditions.

The present study aims to address these knowledge gaps by systematically studying both the dynamic and static flocculation mechanisms in N326 carbon black-filled isoprene rubber systems. Using rheological testing, we examined the influence of small strains on dynamic flocculation behavior. We further characterized the static flocculation mechanisms

through a detailed analysis of the pure rubber properties, particle aggregation states, and bound rubber content. Our study suggests higher flocculation degrees under dynamic conditions compared to corresponding static flocculation. In addition, dynamic flocculation appears to be driven by enhanced particle motion under small shear strain, promoting filler agglomeration.^[20] In contrast, static flocculation primarily involves polymer chain motion, as evidenced by the substantial increase in the bound rubber content. Analysis of both mesoscopic and microscopic filler states suggests that filler particle motion plays only a minor role in static flocculation processes.

EXPERIMENTAL

Materials

The materials used in this study included isoprene rubber (IR, SKI-3S, Russia) with a *cis*-content of 96.3%, a weight-averaged molecular weight of 8.1×10^5 g/mol, and a polydispersity index of 2.9. Carbon black CB (N326) with a primary particle size of approximately 35 nm and a density of 1.8 g/cm³ was supplied by Cabot Co., Ltd., USA. Other additives included zinc oxide (ZnO) from Jiaying Beihua Polymer Auxiliary Co., Ltd. (China), stearic acid (SA) from Tianjin Wilmar Oil Technology Co., Ltd. (China), and *n*-isopropyl-*N*'-phenyl-*p*-phenylenediamine (4010NA) from Tianjin Kemal Chemical Co., Ltd. (China). Toluene solvent used for the extraction experiments was obtained from Xilong Scientific Co., Ltd. (China). All the chemicals were used as received without further purification.

To mimic industrial formulations and ensure that no crosslinking occurred during the flocculation process, cure activators (SA and ZnO) and anti-degradant (4010NA) were added to the formulation, but no curatives were included. The formulations of uncured composites are summarized in Table 1.

Table 1 Formulation of uncured N326 carbon black-filled isoprene rubber composites.

Component	Loading (phr*)
Isoprene rubber (IR)	100.0
Carbon black (N326)	52.0
Zinc oxide (ZnO)	5.0
Stearic acid (SA)	2.0
Antioxidant 4010NA	1.5

*phr: parts per hundred rubber by weight.

Sample Preparation

The CB/IR compounds were prepared using a 1.5-L internal mixer (SS-RPMS-01, Songshu Testing Instrument Co., Ltd, China). A two-stage mixing method was employed to ensure uniform dispersion of carbon black in the rubber matrix.

In the first stage, the raw rubber was masticated for 30 s at 70 °C and 60 r/min (revolutions per minute). Subsequently, ZnO, SA, 4010NA, and half of the CB were added and mixed for 30 s. The remaining CB was then added and the mixture was mixed for 9 min. The compound was dumped and calendared into a 2-mm sheet using a two-roll mill (Songshu Testing Instrument Co., Ltd, China). The total mixing time for the first stage was 10 min and the dump temperature was ap-

proximately 130 °C. The compounds were stored at room temperature for 12 h before proceeding to the second stage.

In the second stage, the compound was preheated in an oven at 75 °C for 10 min to prevent it from stalling in the mixer. The heated compound was then added to an internal mixer at 70 °C and 30 r/min for 2 min. Finally, the compound was calendered into a 2-mm sheet using a two-roll mill. All the samples used in this study were unvulcanized to avoid crosslinking during flocculation.

To ensure the comparability of rheological properties between the filled compounds and pure polymer matrix, pure IR samples were also prepared following the same two-stage mixing process, except that no fillers or additives were included in the formulation. This approach allowed us to isolate the contribution of the rubber matrix to the overall Payne effect in filled compounds. By subtracting the Payne effect of pure rubber from that of the filled compounds, we could more accurately evaluate the contribution of the filler network to the dynamic mechanical behavior.

Characterizations

Micro- and meso-aggregation state analysis

The aggregation state of carbon black was characterized at two levels: microaggregation (nanometer scale) and meso-aggregation (micrometer scale). For microaggregation, the typical length scale is less than 1 μm .^[42] To characterize the microaggregation state, transmission electron microscopy (TEM, JEM-1400Flash, JEOL, Japan) was used at an acceleration voltage of 120 kV. The sample was first frozen at −130 °C and then sliced into ultrathin sections (approximately 100 nm thick) using an ultramicrotome (Leica Ultracut R). Before TEM observation, a small amount of gold colloidal solution (GCN005, BB International Ltd., UK) was dropped onto the ultrathin sections as markers for locating the same area after flocculation. The density distribution function of the CB particles was calculated using a custom-developed image analysis toolkit, which extracts the positions of the filler particles from the TEM images and computes the radial distribution function (RDF) to quantify the aggregation state. The RDF provides a statistical measure of the probability of finding a particle at a given distance from a reference particle, allowing for detailed analysis of the spatial arrangement of CB aggregates.

At the mesoscale, the agglomerates have sizes ranging from a few micrometers to tens of micrometers. To characterize the meso-aggregation state, disperGRADER™ aview (DGAV, Alpha Technologies Co., USA) was used. This instrument measures the average size, number of agglomerates, and white area (the ratio of the area occupied by directly visible agglomerates to the total measurement area) according to ISO 11345-2006. The combination of the TEM and DGAV results provides a detailed understanding of the structural evolution of CB during flocculation.

Bound rubber content measurement

The bound rubber content was measured to evaluate the changes at the filler-polymer interface during flocculation, which was defined as the percentage of rubber chains strongly adsorbed on the filler surface relative to the total rubber content in the system. The contents of total bound rubber (including both tightly bound and loosely bound rubber) and tightly

bound rubber (including only the glassy layer and secondary layer) were determined by immersing the compounds in toluene at different temperatures. The unbound rubber (non-adsorbed rubber chains) was extracted using the solvent, and the loosely bound rubber content was calculated as the difference between the total and tightly bound rubber content.

To measure the total bound rubber content, the compounds were cut into small pieces and immersed in toluene at 25 °C for 14 days in a fume hood. During this process, only the unbound rubber was extracted into the solvent, whereas the tightly bound and loosely bound rubber remained in the solid phase. After immersion, the samples were dried overnight at room temperature to remove residual solvent and then dried in a vacuum oven at 80 °C to a constant weight. The total bound rubber content was calculated based on the weight of the remaining solid phase.

To measure the tightly bound rubber content, the compounds were immersed in toluene at 80 °C for 8 days in a sealed flask. The higher temperature allowed not only the unbound rubber, but also the loosely bound rubber to be extracted into the solvent. The remaining solid phase contains only tightly bound rubber (glassy and secondary layers). After immersion, the samples were dried to a constant weight in a vacuum oven at 80 °C. The tightly bound rubber content was calculated based on the weight of the remaining solid phase. The loosely bound rubber content was determined by subtracting the tightly bound rubber content from the total bound rubber content. The bound rubber content (BR(%)) was calculated using the following equation,^[38]

$$\text{BR}(\%) = \frac{100 \times [W_{\text{fg}} - W_t [m_f / (m_f + m_r)]]}{W_t [m_r / (m_f + m_r)]} \quad (1)$$

where W_{fg} is the weight of the filler and rubber (remaining solid phase after extraction), W_t is the weight of the sample before extraction, m_f is the fraction of filler in the compound, and m_r is the fraction of rubber in the compound.

In addition, the glassy-bound rubber content was determined using time-domain nuclear magnetic resonance (TD-NMR) on a Bruker minispec mq20 series spectrometer. The short echo time in the magic-sandwich echo (MSE) sequence was used to measure the relaxation of the glassy layer at the interface.^[43]

Rheological testing

The flocculation behavior of the compounds was characterized using a rubber process analyzer (RPA Elite, TA Instruments). Both the static and dynamic flocculation processes were investigated to understand the influence of temperature and strain on filler network formation.

To study the static flocculation behavior, the compounds were annealed at temperatures ranging from 25 °C to 145 °C (8 temperature points were collected, *i.e.*, 25, 60, 70, 80, 90, 100, 120, and 145 °C) in an oven for 7 h. During this process, no external strain was applied, allowing the filler network to evolve under thermal conditions. After annealing, the samples were removed from the oven and equilibrated in the RPA at 25 °C with an oscillatory strain of 0.1% for 10 min to ensure a consistent testing temperature. A strain sweep was performed between 0.05% and 20% at a frequency of 1 Hz to evaluate the extent of flocculation.

To study the dynamic flocculation behavior, the compounds were directly subjected to a small oscillatory strain (0.1%) at 8 different temperatures (25, 60, 70, 80, 90, 100, 120, and 145 °C) in the RPA for 7 h. During this process, the storage modulus G' was monitored in real-time to track the evolution of the filler network under a small oscillatory strain. After the dynamic flocculation process, the temperature was adjusted to 25 °C and the samples were equilibrated at a small oscillatory strain of 0.1% for 10 min to ensure a consistent testing temperature. A subsequent strain sweep was performed between 0.05% and 20% at a frequency of 1 Hz.

To estimate the degree of flocculation, we calculated the magnitude of the Payne effect, which quantifies the extent of the breakdown of the filler network during strain sweeps. The Payne effect was evaluated as the difference between the plateau modulus (G'_0 , defined as the average G' in the linear region) and the modulus at a large strain (20% in this study):

$$\Delta G' = G'_0 - G'_{\gamma=20\%} \quad (2)$$

We further calculated the flocculation degree (D_f) as the difference between the magnitude of the Payne effect at a given temperature and that at 25 °C.^[44]

$$D_f = \Delta G'(T) - \Delta G'(25\text{ °C}) \quad (3)$$

By comparing the results of static and dynamic flocculation, we can distinguish the contributions of thermal annealing and a small oscillatory strain to the evolution of the filler network. The static flocculation process primarily reflects the influence of temperature on filler aggregation, whereas the dynamic flocculation process captures the combined effects of temperature and small strain on filler network formation.

In addition to flocculation behavior, the contribution of the rubber matrix to the overall mechanical behavior during static flocculation can also be obtained from the rheological test of pure rubber. For a better comparison, pure rubber was first annealed at different temperatures in the same manner as static flocculation. The sample was then equilibrated at 25 °C for 10 min in RPA; subsequently, a strain sweep was performed between 1% and 200% at a frequency of 1 Hz. The contribution of the rubber matrix can be evaluated using the modulus at small strains.

Molecular weight analysis

To investigate the potential degradation of the polymer chains during the static annealing process, the molecular weights of the polymers extracted from both the annealed compounds and identically processed pure IR were determined by gel permeation chromatography (GPC, Agilent Technologies). GPC measurements were conducted at 35 °C in a polystyrene standard with a PL-GPC50 system equipped with a PL gel Mined-B LS column using tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min. The polymer was extracted from the annealed samples by dissolving the samples in THF, and the polymer solutions were filtered through a PTFE membrane (1 μm pore size) prior to GPC analysis. The filtered polymer solution was then injected into the GPC system to obtain number-average molecular weight (M_n). Each sample was measured three times to ensure accuracy.

Particle diffusion analysis

To evaluate the particle diffusion distance during static floccula-

tion, we calculated the diffusion coefficient D using the Stokes-Einstein equation. This equation is often employed to describe the diffusion behavior of spherical and rigid particles in dilute solutions. In CB-filled IR systems, the filler-filler and filler-matrix interactions cannot be ignored. Despite these complexities, the SE equation still provides a theoretical upper-bound estimate for the maximum diffusion distance of the filler particles within the matrix. Diffusion coefficient D was calculated using the following SE equation:

$$D = \frac{kT}{6\pi\eta a} \quad (4)$$

where k is the Boltzmann constant, T is the absolute temperature, η is the polymer matrix viscosity (viscosity is estimated from the slope of the shear stress versus shear rate curve at small shear rates from the strain sweep test), and a radius of the particle. Given diffusion time t , the diffusion distance r was estimated using the one-dimensional mean-square displacement (MSD) formula:

$$r = \sqrt{2Dt} \quad (5)$$

RESULTS AND DISCUSSION

In this study, we systematically investigated the flocculation behavior of N326 CB-filled IR compounds under both dynamic and static conditions. We combined rheological testing, microscopic characterization, and bound-rubber content analysis to elucidate the mechanisms governing static flocculation. The following sections present a detailed analysis of the contribution of the rubber matrix, evolution of filler aggregation states, and changes in the bound rubber content, providing a proposed mechanism for static flocculation.

Comparison of Dynamic and Static Flocculation Behavior

To investigate the influence of a small shear strain on the flocculation process, we compared the dynamic and static flocculation behaviors of CB/IR compounds. Fig. 1(a) shows the time-dependent G' during dynamic flocculation at different temperatures, under a small oscillatory strain of 0.1%. G' increased rapidly within the first 2 h and continued to rise gradually over the 7-h period, indicating that the flocculation process continued across a broad range of timescales. A rapid increase in G' within the first 2 h has been reported in several studies.^[21,31,40] When the filler portion reached 52 phr, a strain of 0.1% during the dynamic flocculation process increased the particle mobility. Thus, at the initial stage, the faster formation of particle aggregates leads to a rapid increase in G' , followed by a slower assembly into a robust filler network.^[45] It is clearly seen that G' did not decrease with increasing temperature in the range of 25–90 °C, suggesting that the promotion of flocculation outweighed the temperature-induced decline in modulus in this temperature range.

To quantify the dynamic Payne effect, we performed strain sweeps on rubber compounds after dynamic flocculation at various temperatures. Fig. 1(b) shows the strain sweep curves of the samples at 25 °C after dynamic flocculation. The curves exhibit the typical Payne effect, where G' remains nearly constant at small strains (linear region, 0.05% to 0.2% strain in this section) and decreases significantly at larger strains (non-

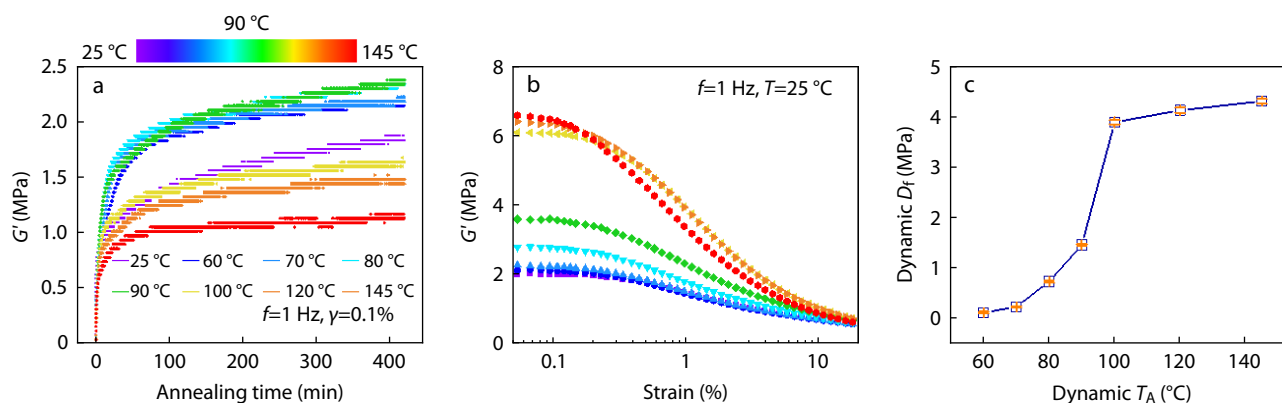


Fig. 1 Dynamic flocculation in small strain of compounds. (a) Flocculation behavior of compounds without curatives at different temperatures; (b) Subsequent strain sweeps at 25 °C; (c) Flocculation degree (D_f) as a function of annealing temperature T_A .

linear region). The plateau modulus increased with annealing temperature, indicating the formation of a more robust filler network during dynamic flocculation.

Fig. 1(c) shows the dynamic flocculation degree as a function of annealing temperature. The dynamic flocculation degree increased rapidly below 100 °C and reached approximately 4.3 MPa at 145 °C, indicating that the application of a small shear strain significantly enhanced filler agglomeration. This suggests that the motion of the filler particles can be improved under oscillatory strain to form a more robust filler network.

In contrast, the static flocculation process without applied strain exhibited a different trend. Fig. 2(a) shows the strain sweep curves of the samples after static annealing, which display the typical Payne effect. The plateau modulus initially increased with temperature, reaching a maximum at 90–100 °C, but decreased significantly when the temperature exceeded 100 °C. To quantitatively compare static and dynamic flocculation, we calculated the static flocculation degree using a similar method, in which the plateau modulus was averaged over the linear region (0.05%–0.26% strain). As shown in Fig. 2(b), the maximum static flocculation degree reached approximately 0.19 MPa at 90–100 °C, an order of magnitude lower than the dynamic flocculation degree (4.3 MPa at 145 °C). This phenomenon occurs because the static flocculation process can be regarded as in an equilibrium state, and the rearrangement of the filler network becomes slow, resulting in a minimal change in the elastic modulus of the rubber. This result suggests the critical role of a small shear strain in enhancing filler network formation during dynamic flocculation.

At temperatures above 100 °C, the static flocculation degree decreased significantly, likely due to the thermal degradation of the polymer chains, which weakened the filler-polymer interface. In percolated rubber nanocomposites, the filler network can reform under small strains during dynamic flocculation, leading to a robust Payne effect.^[21] However, in the absence of shear, static flocculation relies primarily on the evolution of the filler-polymer interface rather than on filler aggregation. This mechanism explains why the static flocculation degree is much lower than its dynamic counterpart, and why it declines at high temperatures, where polymer degradation outweighs interfacial reinforcement. A detailed discussion of the polymer chain degradation during high-tempera-

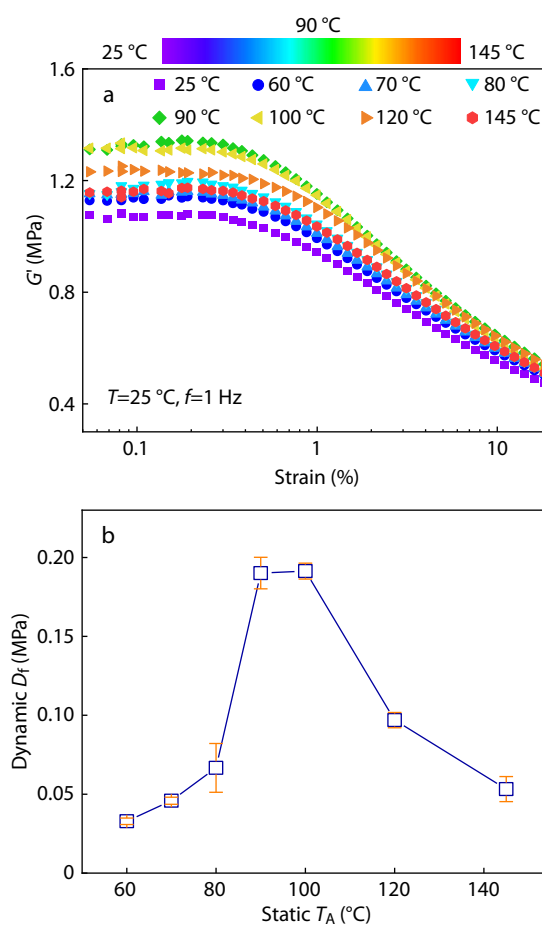


Fig. 2 (a) The strain sweep curves of the compounds after static annealing at different temperatures; (b) Static flocculation degree as a function of annealing temperature.

ture flocculation is presented in the following sections.

Contribution of the Rubber Matrix to the Modulus

To isolate the contribution of the rubber matrix to the overall mechanical behavior of the CB/IR compounds, we examined the nonlinear viscoelastic properties of pure IR after static annealing at different temperatures. Fig. 3(a) shows the strain amplitude dependence of the storage modulus for pure IR after static an-

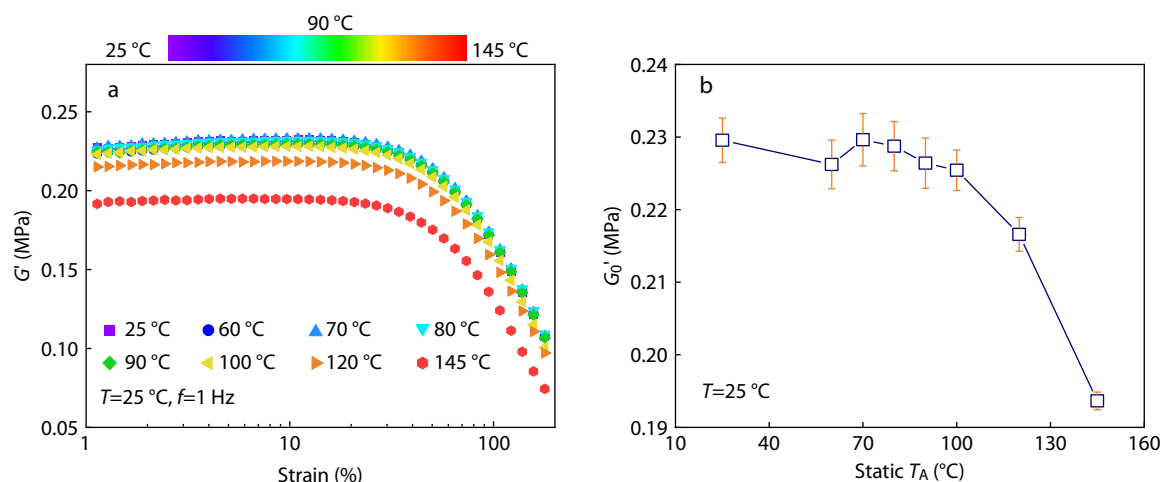


Fig. 3 (a) G' as a function of strain amplitude γ for the pure rubber after annealing at different temperatures; (b) G'_0 of pure rubber as a function of annealing temperature.

nealing at temperatures ranging from 25 °C to 145 °C. Pure rubber exhibited the typical Payne effect, with G' remaining nearly constant in the linear region ($\gamma < 40\%$) and decreasing significantly in the nonlinear region ($\gamma > 40\%$). The critical strain amplitude for pure IR is much higher than that of the filled compounds, which was attributed to the strain amplification effect caused by the presence of rigid filler particles in the filled system.^[46,47]

To quantify the plateau modulus of pure IR, we calculated the average G' in the linear region (1%–20% strain) for each static annealing temperature, and the results are shown in Fig. 3(b). The nearly constant G'_0 in the range of 25–100 °C indicates that the polymer chains were thermally stable within this temperature range. However, when the annealing temperature exceeded 100 °C, G'_0 decreased significantly, suggesting that this temperature may be the onset of thermal degradation in the polymer matrix. This degradation is consistent with the known behavior of isoprene rubber, which contains unsaturated double bonds that are susceptible to chain scission at elevated temperatures.^[48]

To further confirm the thermal degradation of the polymer chains, we analyzed the molecular weight of the polymer extracted from the statically annealed compounds using GPC. Fig. 4 shows the M_n of the extracted polymer as a function of static annealing temperature. M_n remained relatively constant from 25 °C to 100 °C, but decreased sharply at higher temperatures, particularly above 100 °C. This decrease in molecular weight is a clear indication of polymer chain scission, which is consistent with the observed decline in G'_0 at high temperatures. The molecular weight of the annealed pure IR under the same processing conditions was also measured, and the results are shown in Fig. S1 (in the electronic supplementary information, ESI). Similar to the extracted polymer, the molecular weight of pure IR decreases with increasing annealing temperature, indicating that thermal degradation also occurs in the polymer matrix.

Thermal degradation of the polymer matrix has important implications for the flocculation behavior of filled compounds. In the static flocculation process, the decrease in G'_0 of the rubber matrix at high temperatures (above 100 °C) co-

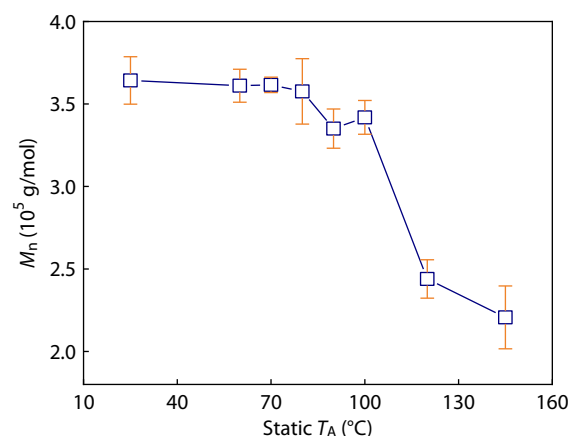


Fig. 4 The number-average molecular weight of polymer extracted from the compounds as a function of annealing temperature.

incided with a reduction in the flocculation degree (Fig. 2b). This suggests that the breaking of the polymer chains weakens the filler-polymer interface, leading to a less robust filler network and a lower flocculation degree. However, it is important to note that even at high temperatures, the flocculation degree remained higher than that observed at lower temperatures (60–80 °C), indicating that other factors, such as the increase in bound rubber content, may partially compensate for the effects of polymer degradation.

Evolution of Filler Aggregation State

To explore the structural evolution of filler particles during flocculation, we characterized the morphology of the CB aggregates and agglomerates before and after annealing using TEM and DGAV. This analysis aimed to determine whether filler particle motion plays a significant role in the static flocculation process, particularly in the absence of an external strain.

Micro-aggregation state analysis

The microaggregated state of the CB particles was characterized using TEM. Fig. 5 shows TEM images of the CB/IR compounds from the same ultrathin section before and after static

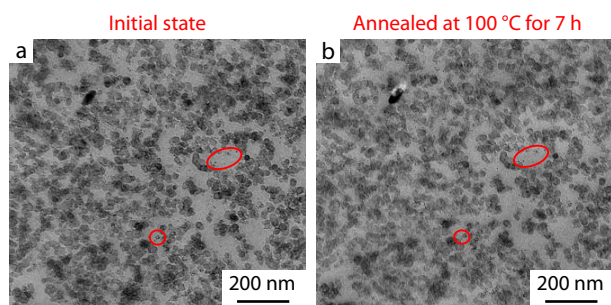


Fig. 5 TEM images of IR/N326 compounds from the same ultrathin section (a) before annealing and (b) after annealing at 100 °C for 7 h. The small dark dots in the images, such as those in the red circle, are the gold particles for localization.

annealing at 100 °C for 7 h. To ensure an accurate comparison, gold nanoparticles were used as markers to locate the same area before and after flocculation. As shown in Figs. 5(a) and 5(b), no apparent movement of the CB aggregates was observed, indicating that the filler particles remained relatively stationary during static flocculation. This result is consistent with previous studies, which also reported negligible filler particle motion during thermal aging in the absence of external strain.^[40]

To avoid the limitation of ultrathin section thickness on particle motion during the flocculation process, the samples before flocculation and after flocculation were sliced into sections and characterized by TEM; the results are shown in Figs. 6(a) and 6(b). To further quantify the spatial arrangement of CB particles, we calculated the RDF using a custom-devel-

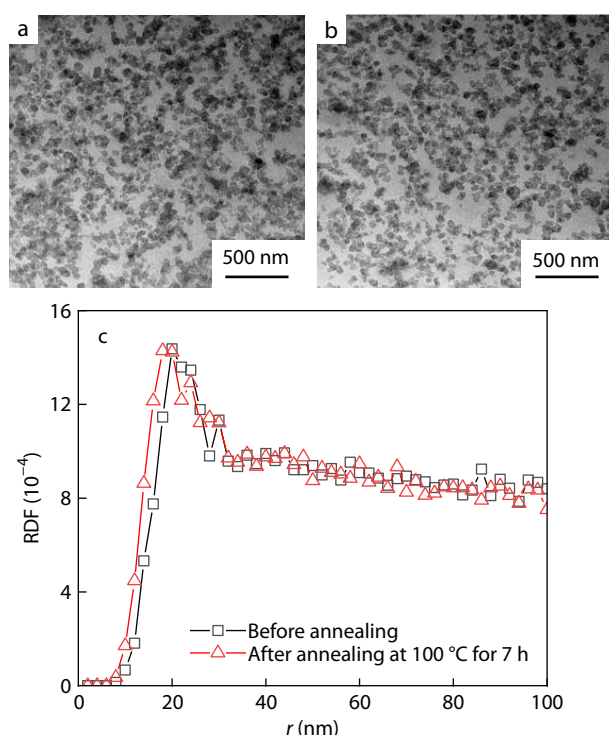


Fig. 6 Typical TEM images of IR/N326 compounds (a) before annealing and (b) after static annealing at 100 °C for 7 h; (c) RDF of CB fillers in the composites before and after annealing. The RDF was calculated by the average of five randomly selected TEM images.

oped image analysis toolkit that describes the probability of finding another particle within a given distance (r) from a reference filler particle.^[49] Fig. 6(c) compares the RDF results of the samples before and after static flocculation. Interestingly, the first peak of the RDF, corresponding to the most probable interparticle distance, shifted slightly from approximately 20 nm to 18 nm after annealing. This observation suggests that, while the CB aggregates maintain their overall structural integrity, they undergo subtle rearrangements that lead to a more compact configuration with slightly improved local ordering. However, the overall shape and intensity of the RDF curves remained largely unchanged, indicating that the motion of CB particles was highly constrained and did not result in significant agglomeration or rearrangement. The results indicate that the filler particles experienced limited mobility during the static flocculation process, resulting in a modest enhancement of particle dispersion.

Meso-aggregation state analysis

At the mesoscale, the aggregation state of CB particles was characterized using DGAV, which measures the average size, number, and distribution of agglomerates in the range of 2.9–57 μm . Fig. 7(a) shows the mean agglomerate size and white area as a function of static annealing temperature. Both the mean agglomerate size and white area slightly decreased with increasing static annealing temperature. This suggests that the filler particles did not significantly aggregate during static flocculation. Instead, the dispersion of the fillers improved, implying the dominant role of polymer relaxation during static annealing.

The histogram distribution of agglomerate sizes (Fig. 7(b)) also shows a decreased distribution of larger agglomerates at higher static annealing temperatures. This implies that larger agglomerates may be redistributed during annealing because of the motion of the polymer chains at higher temperatures. This result agrees with previous studies, which showed that no agglomeration occurred during aging at 200 °C for 5 days, with only a small number of larger particles breaking into smaller agglomerates.^[34]

Changes in Bound Rubber Content

To elucidate the changes at the filler-polymer interface during static flocculation, we measured the bound-rubber content of the samples after annealing at different temperatures. Bound rubber, which refers to the portion of rubber chains strongly adsorbed on the filler surface, is a critical indicator of the strength of the filler-polymer interactions. The evolution of bound rubber content during flocculation provides valuable insights into the mechanisms governing the formation and stability of the filler network.

Total bound rubber content

The total bound rubber content was measured by immersing the compounds in toluene at 25 °C for 14 days. During this process, the unbound rubber (non-adsorbed rubber chains) was extracted into the solvent, whereas the bound rubber (both tightly bound and loosely bound) remained in the solid phase. Fig. 8(a) shows the total bound rubber content as a function of annealing temperature. The total bound rubber content increased from 23% to 28% as the temperature increased from 25 °C to 145 °C, indicating that the interactions between the polymer

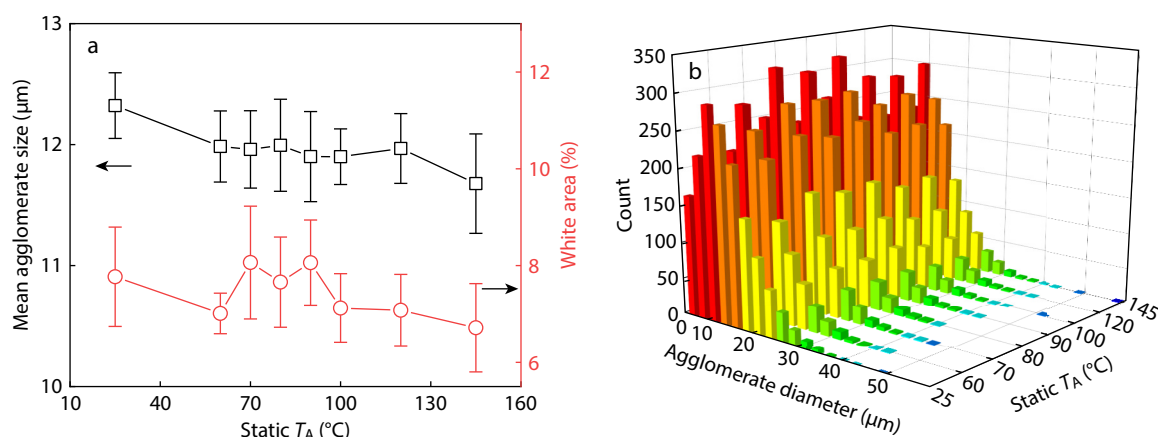


Fig. 7 Filler dispersion before and after flocculation. (a) Mean agglomerate size and the white area of filler agglomerates; (b) Size distribution of filler agglomerates in the range of 2.9–57 μm.

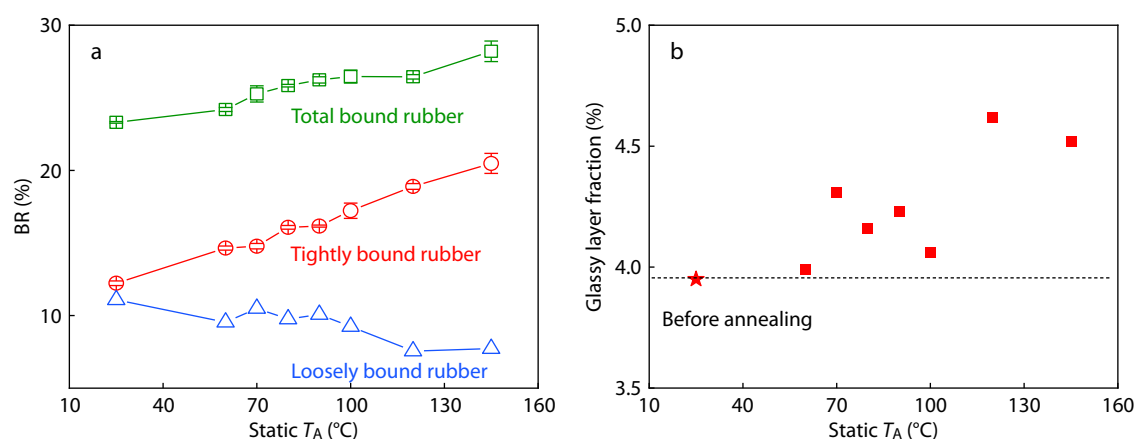


Fig. 8 Variations of (a) total bound rubber, tightly bound rubber, loosely bound rubber, and (b) glassy-bound rubber as a function of static annealing temperature.

chains and carbon black surface became stronger at higher temperatures.

According to Meissner's bound rubber model,^[50] the bound rubber content may decrease owing to the decrease in the molecular weight at higher annealing temperatures (Fig. 4). However, in this study, the total bound rubber content increased with increasing temperature, which can be attributed to several factors. First, the degradation of polymer chains at high temperatures (above 100 °C) generates free radicals that are rapidly trapped by carbon black, leading to the formation of additional bound rubber.^[51] However, at elevated temperatures, the movement of the polymer chains increases significantly toward entropy maximization. Owing to the high filler filling, the chains became topologically confined within the percolated filler network, resulting in chain adsorption on the filler surface. The increase in bound rubber outweighs its decrease, resulting in a net increase in bound rubber content with increasing temperature. These findings are consistent with those of previous studies, which have reported that the bound rubber content increases with temperature due to enhanced polymer chain adsorption and chemical interactions at the filler-polymer interface.^[52]

Tightly bound rubber content

The tightly bound rubber content, which includes the glassy

layer and secondary layer bound rubber, was measured by immersing the compounds in toluene at 80 °C for 8 days. The higher temperature and extended immersion time allowed not only the unbound rubber, but also the loosely bound rubber to be extracted into the solvent. Fig. 8(a) shows that the tightly bound rubber content increased by approximately 8% over the temperature range of 25–145 °C, which is a larger increase compared to the total bound rubber content. This suggests that the tightly bound rubber, particularly the secondary layer, plays a dominant role in the evolution of the filler-polymer interface during static flocculation.

The increase in the tightly bound rubber content is likely due to the replacement of short polymer chains by longer chains at the interface.^[53] As the temperature increased, the mobility of the polymer chains improved, allowing longer chains to diffuse to the filler surface and form stronger interactions. This process is supported by the molecular weight analysis presented in Fig. 4, which shows a significant decrease in the molecular weight of the extracted polymer at high temperatures, indicating that shorter chains are preferentially extracted into the solvent.

Loosely bound rubber content

The loosely bound rubber content was calculated as the difference between the total bound and tightly bound rubber con-

tents. As shown in Fig. 8(a), the loosely bound rubber content decreases with increasing temperature, particularly above 100 °C. This decrease is consistent with the idea that loosely bound rubber is gradually replaced by tightly bound rubber as temperature increases. The replacement of loosely bound rubber by tightly bound rubber reflects the strengthening of the filler-polymer interface, which is a key factor in the increase in the flocculation degree during static annealing.

Glassy-bound rubber content

The glassy-bound rubber content, which represents the most strongly adsorbed polymer chain on the filler surface, was measured using TD-NMR. Fig. 8(b) shows the glassy-bound rubber content as a function of annealing temperature. The glassy-bound rubber content remained relatively constant at temperatures below 60 °C but slightly increased at higher temperatures, reaching a maximum of 4.6% at 120 °C. This increase is attributed to the degradation of polymer chains at high temperatures, which releases free radicals that are quickly trapped by the carbon black surface, leading to the enhanced adsorption of polymer chains.^[51]

However, the overall increase in the glassy-bound rubber content was less than 1%, indicating that the growth of tightly bound rubber (8%) was primarily due to the increase in the secondary layer rather than the glassy layer. This finding suggests that the secondary layer plays a more significant role in the reinforcement of rubber nanocomposites than the glassy layer does.

Implications for flocculation mechanism

The changes in the bound rubber content during static flocculation provided critical insights into the mechanisms governing the evolution of the filler-polymer interface. The increase in the total bound rubber content, particularly the tightly bound rubber, reflects the strengthening of the interfacial interactions between the polymer chains and the carbon black surface. This strengthening is driven by the enhanced mobility of the polymer chains at higher temperatures and the degradation of the polymer chains, which generates additional adsorption sites on the filler surface.

The decrease in loosely bound rubber content and the slight increase in the glassy-bound rubber content further support the idea that the filler-polymer interface becomes more robust during static flocculation. These changes in bound rubber content are consistent with the observed increase in flocculation degree, particularly at temperatures below 100 °C. At higher temperatures, the degradation of polymer chains weakens the filler-polymer interface, leading to a reduction in flocculation degree. However, the overall increase in the bound rubber content suggests that the strengthening of the interfacial interactions partially compensated for the effects of polymer degradation.

In summary, the evolution of bound rubber content during static flocculation highlights the critical role of the filler-polymer interface in the formation and stability of the filler network. The increase in tightly bound rubber content, particularly in the secondary layer, is the primary driver of the increase in the flocculation degree, while the glassy-bound rubber plays a relatively minor role. These findings provide valuable insights into the mechanisms governing static floccula-

tion and offer guidance for optimizing the interfacial interactions in rubber nanocomposites.

Mechanism of Static Flocculation in CB/IR Compounds

Based on the experimental results presented in the previous sections, we proposed a polymer-dominated mechanism for static flocculation in CB/IR compounds. This mechanism highlights the critical role of polymer chain motion and interfacial interactions in driving filler network evolution, with negligible contribution from filler particle movement. The following discussion integrates the key findings from rheological testing, microscopic characterization, and bound rubber content analysis to unravel this mechanism.

To explain the limited motion of CB particles during static flocculation, we calculated the diffusion distance using Eqs. (4) and (5). For CB aggregates with a diameter of 200 nm and a polymer matrix viscosity of $\eta = 2.56 \times 10^4$ (Pa·s) at 100 °C, the maximum diffusion distance r over 7 h was approximately 73 nm.

This limited diffusion distance of filler aggregates is further reduced owing to the existence of a densely packed filler network (52 phr CB loading) in the system. Within the dense filler network, the interparticle spacing was significantly reduced, leading to pronounced steric hindrance that severely restricts particle diffusion. The close packing of particles also amplifies the van der Waals interactions between adjacent fillers, making it highly unlikely that filler particles undergo significant agglomeration during static flocculation. In addition, this constraint is further amplified by the physical entanglement of polymer chains adsorbed on the CB surfaces and the gradual thickening of interfacial layers, creating a molecular "cage" that effectively traps filler particles. Such conditions prohibit large-scale particle rearrangement, leaving only subtle localized movements driven by thermal fluctuations in the polymer matrix.^[20]

While the filler particles remained essentially static, the polymer chains underwent profound reorganization. At higher temperatures (approximately 100 °C), the relaxation time of the rubber polymer chains is in the range of several hundreds of seconds,^[54] allowing the polymer chains to fully relax during annealing. This thermal activation enables the polymer chains to disentangle, diffuse toward the filler surfaces, and establish stronger interfacial bonds. The consequence was a systematic increase in the bound rubber content from 23% at 25 °C to 28% at 145 °C, as detected through solvent extraction experiments. Notably, the growth of tightly bound rubber (secondary layer) accounts for most of this increase, suggesting that longer polymer chains progressively replace shorter chains at the interface. Even when thermal degradation cleaves the polymer backbones above 100 °C, the newly generated chain ends appear to participate in interfacial interactions, partially offsetting the mechanical weakening caused by chain scission.

This stark contrast with dynamic flocculation underscores the possibility of this polymer-dominated mechanism. Oscillatory shear strains of 0.1% mobilize filler particles to build extensive networks (flocculation degree 4.3 MPa at 145 °C), while static conditions mainly rely on polymer chain mobility

to modify interfacial architecture. This dependency explains why static flocculation peak (90–100 °C) is just 0.19 MPa, then declines as chain degradation dominates over interface reinforcement, a temperature threshold absent in shear-assisted dynamic processes.

The proposed polymer-dominated mechanism for static flocculation may have key implications for the processing and performance of rubber nanocomposites. In industrial applications, rubber compounds are often stored for extended periods before further processing or vulcanization. Static flocculation can occur during this storage period, leading to changes in the mechanical properties of the material. Our findings suggest that the evolution of the filler network during storage is primarily driven by the motion of the polymer chains and the strengthening of the filler-polymer interface rather than the movement of filler particles. By connecting the fundamental understanding and processing realities, this work can bridge the gap between nanoscale interfacial phenomena and macroscale rubber performance.

CONCLUSIONS

In this study, we systematically investigated the flocculation behavior of N326 carbon black-filled isoprene rubber compounds under both dynamic and static conditions. We found that dynamic flocculation is driven by the motion of filler particles under a small shear strain, leading to significant filler agglomeration and a pronounced Payne effect. However, static flocculation is primarily governed by the motion of the polymer chains and the evolution of the filler-polymer interface. The negligible movement of CB particles, as evidenced by TEM and DGAV, suggests that filler particle motion plays only a minor role. Instead, the increase in flocculation degree is attributed to the increase in bound rubber content, particularly tightly bound rubber, which strengthens the interfacial interactions. The proposed polymer-dominated mechanism for static flocculation provides new insights into the evolution of filler networks during industrial storage and processing.

In conclusion, this study enhances our understanding of the mechanisms governing flocculation in CB-filled rubber nanocomposites and offers practical guidance for controlling the filler network structure under tailored processing conditions. Note that the filler loading in our present work was high, which may have led to decreased mobility of the filler particles during flocculation. Future studies could explore the effects of different filler types, filler loadings, polymer matrices, and processing parameters on flocculation behavior, further advancing the development of high-performance rubber materials.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. The authors' contact information: qqgu@mail.ustc.edu.cn (Q.Q.G.), zysun@ciac.ac.cn (Z.Y.S.)

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