

Enhancing the electrical conductivity of incompatible polymer blends

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A novel two-step mixing process is investigated, in which carbon black fillers are added to a nitrile butadiene rubber/ethylene propylene diene monomer mixture in different sequences.

To improve the mechanical properties of an elastomer matrix, it is common practice to add carbon black as a filler material. Carbon black (CB) is also often added to insulating polymers to produce semiconducting and antistatic compounds. In addition, other conductive fillers (including carbon nanotubes and graphene) can be added to insulating polymers to turn the resulting blends into conductive composites.¹⁻³ It remains a challenge, however, to develop conductive polymer composites that have good filler dispersions as well as good mechanical, thermal, and electrical properties.

The distribution characteristics of carbon fillers (such as carbon nanotubes) have been a major topic of interest during the last decade. Indeed, it has been shown that the distribution and dispersion of fillers within rubber blends are key factors that affect various physico-mechanical properties of the materials (e.g., the tensile strength, elongation at break, modulus, and conductivity).^{4,5} There have been relatively few investigations, however, of the distribution of CB in different blend phases. There are a number of main reasons why CB has not been the focus of many previous studies. For example, a substantially greater amount of CB is required to improve the mechanical and electrical properties of blends (compared with other filler materials). Moreover, optical and morphological techniques for studying the affinity of CB toward a particular phase in blend systems become very difficult for high CB loadings.

In this work,⁶ we have thus investigated the preferential distribution of CB into the immiscible phases of a rubber blend, and how this controls the mechanical and electrical properties of the blend. Specifically, we have studied the dispersion of high-abrasion furnace CB within a nitrile butadiene rubber (NBR)/ethylene propylene diene monomer (EPDM) blend (in a 50/50 ratio). We chose these two rubbers because of the wide difference in their polarity and Mooney viscosity values.^{7,8}

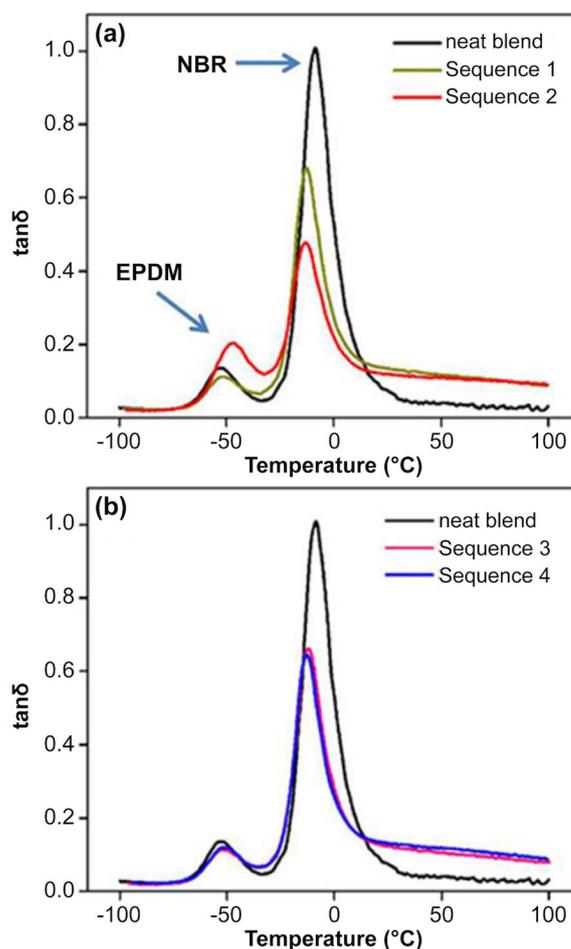


Figure 1. Temperature sweep results for a neat blend of nitrile butadiene rubber (NBR) and ethylene propylene diene monomer (EPDM), as well as for (a) the sequence 1 and 2 blends and (b) the sequence 3 and 4 blends (see Table 1) that contain 50 parts per hundred (phr) carbon black (CB). Results are given in terms of the $\tan\delta$ peak height (a measure of damping).

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Table 1. The four different mixing sequences investigated in this study. Sequence 3 represents a conventional mixing method.

Sequence	Mixing sequence
1	(EPDM+50phr CB) + NBR
2	(NBR+50phr CB) + EPDM
3	EPDM+NBR+ 50phr CB
4	(EPDM+25phr CB) + (NBR+25phr CB)

Table 2. Weight fraction of CB in each phase of the NBR/EPDM blends. The relative proportion of the two phases in each sample is given in parentheses. Information for the sequence 2 sample is excluded because the mathematical formation available in the literature is insufficient to calculate the concentration of CB in the different phases for this composite.

Sequence sample	NBR phase	EPDM phase
1	≈27.5phr (55.0%)	≈18.2phr (36.4%)
3	≈30.7phr (61.4%)	≈18.2phr (36.4%)
4	≈22.0phr (44.0%)	≈13.4phr (26.8%)

Furthermore, this combination of rubbers has received attention in several fields because EPDM exhibits very good weathering behavior and NBR exhibits very good oil and solvent resistance.⁹⁻¹¹

We used an internal mixer to prepare our composite samples (at a temperature of 120°C). In addition, to achieve selective addition of CB in a particular rubber phase, we used a two-step mixing process. In the first step, we pre-blended the first rubber phase with the full amount of CB for three minutes. We chose to use a 50phr (parts per hundred) CB loading because this is below the 60phr percolation threshold (i.e., the critical concentration required to make the system conductive), as determined from DC conductivity measurements. This amount of CB also allowed us to investigate the formation of conductive networks in the samples. We then produced sheets of this rubber/CB mixture in a two-roll mill. In the second stage, we added the second rubber phase to the mixer and subsequently blended this with the first rubber/CB masterbatch (as well as other necessary ingredients, including sulfur, zinc oxide, stearic acid, paraffin oil, 1,2-dihydro-2,2,4-trimethyl quinoline, *N*-cyclohexyl-2-benzothiazylsulfenamide, and *N*-tert-butyl-2-benzothiazyl sulfenamide) for 10 minutes. The four different mixing sequences we investigated are given in Table 1.

We performed a temperature sweep study (a dynamic mechanical test) for all four of our composites, and used the $\tan\delta$ (i.e., damping) results (see Figure 1) and a series of equations to calculate the CB in each phase of the different blends.¹² The $\tan\delta$ measure provides information about the CB distribution in polymer blends, i.e., the peak value

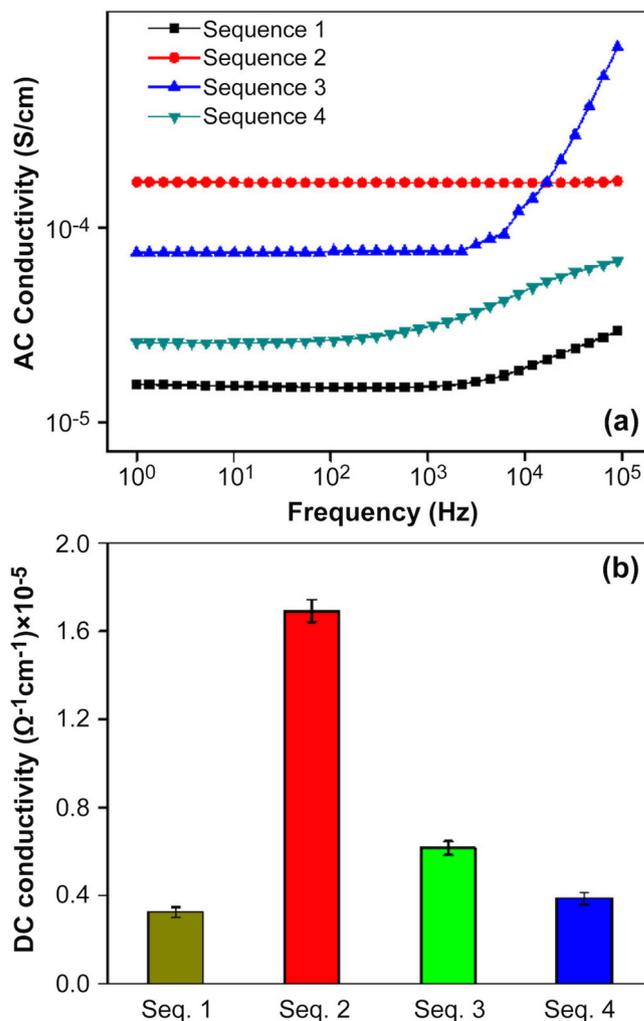


Figure 2. Variation in (a) AC and (b) DC conductivity of the four different sequence (seq.) samples.

decreases with increasing CB concentrations.¹³ Specifically, we determined the weight fraction of CB in both the NBR and EPDM phases of the blends, as well as the proportion of the two phases within each sample (see Table 2). Our results indicate that the CB has a higher affinity toward the NBR phase than the EPDM phase in the blends. We confirmed this finding (i.e., the higher affinity of CB toward the less viscous NBR phase) by conducting a surface energy study and determining (from the Owens-Wendt equation) the work adhesion values for the blend components.⁶

We also measured the AC conductivity of our samples to study the effect of conductive network formation (caused by the preferential distribution of CB in different phases) in our blends. We find—see

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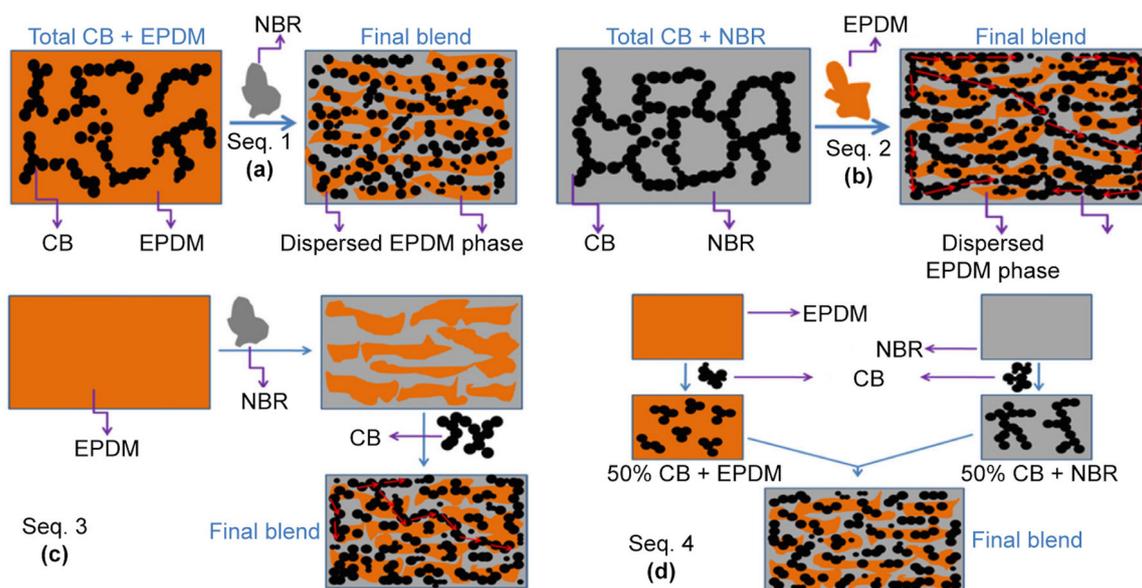


Figure 3. Schematic illustrations of the redistribution of CB within the rubber phases and the formation of conductive (continuous) networks during the (a) sequence 1, (b) sequence 2, (c) sequence 3, and (d) sequence 4 mixing procedures. Red arrows indicate the electron flow path.

Table 3. Mechanical properties of the different mixing sequence samples.

Sequence	Tensile strength (MPa)	Elongation at break (%)
1	10.20±0.5	319±15.9
2	10.02±0.6	282±14.1
3	11.50±0.4	355±17.7
4	10.82±0.6	348±17.4

Figure 2(a)—that the sequence 2 sample generally has the highest conductivity and the widest frequency-independent region of all the samples. The DC conductivity results—see Figure 2(b)—also follow the same trend as the AC conductivity results. We believe that the early incorporation of CB into the low-viscosity NBR matrix (i.e., sequence 2) means that the network structure was retained (confirmed via a hysteresis study) and gave rise to the most conductive system. In contrast, when the CB is added to the higher-viscosity EPDM first (sequence 1 and 4), the CB suffers from a large amount of shearing that causes the CB to break up into smaller particles and gives rise to the low-conductivity blend. Our results thus confirm that CB migration from one phase to another occurs during mixing and affects the formation of the CB networks within the rubber matrix (see Figure 3), which in turn influences both the electrical and mechanical (see Table 3) properties of the samples.

In summary, we have investigated the electrical and mechanical properties of NBR/EPDM blends—produced in four different mixing sequences—that contain 50phr CB. Our in-depth characterizations show that the ideal mixing sequence is to add the CB to the NBR matrix in the first step of mixing, before adding this mixture to the EPDM phase. In this way, the CB particles can be redistributed within the final blend to form a continuous network. The AC and DC conductivity of the sample can thus be improved simultaneously, and is better than that achieved in a conventional mixing method. In addition to the sequence of mixing, the conductivity of the samples is also influenced by the viscosity of the rubber constituents and by the surface energy of the individual components. In our future research we will evaluate the distribution behavior of various types of CB within technologically compatible blends prepared via different mixing sequences, as well as the effect on the electrical conductivity, mechanical properties, and processing behavior of the samples.

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