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Dielectric Properties of Phase Separated Blends containing a Microcapacitor Network of Carbon Nanotubes: Compatibilization by a Random or Block Copolymer

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Abstract

The mechanisms governing the dielectric blend properties at different length scales for phase separating blends with multiwall carbon nanotubes (MWNTs) are unravelled by tuning the microstructure. Thereto, compatibilization by interfacially segregated block copolymers (bcp) and random copolymers (rcp) of poly(styrene-random/block-methyl methacrylate)(PS-r/b-PMMA) was achieved in phase separating blends of poly[(α -methyl styrene)-co-acrylonitrile] and poly(methyl methacrylate) (P α MSAN/PMMA) undergoing spinodal decomposition. In our recent work, we elucidated the effects of copolymer architecture and molecular weight on the percolating network of selectively localized MWNTs. Only short bcp and long rcp/bcp improved the connectivity and refinement of the P α MSAN phase laden with MWNTs and the resulting conductivity. In the present work, we study the effects of copolymer type, architecture and concentration on the dielectric properties. We demonstrate a concurrent increase of the interfacial capacitance and decrease of the interfacial resistance of MWNTs with entrapped P α MSAN upon effective compatibilization. This is attributed to the increasing amount of connected parallel microcapacitor RC elements formed by the network of adjacent MWNTs enclosing a thin dielectric layer of P α MSAN. At high frequencies (above 1 MHz) the electrons hop between the neighboring MWNTs, whereas at intermediate frequencies, the electrons of the MWNTs tunnel through the barriers imposed by the entrapped P α MSAN. The physical characteristics of the microcapacitor network namely the thickness of the microcapacitors and the volume fraction of entrapped P α MSAN contributing to the microcapacitor network are estimated by describing the dielectric relaxation time and strength using the fluctuation induced tunneling model and the interlayer model respectively. Combining the knowledge of the aforementioned parameters allows to describe the evolution of the total interfacial capacitance of the microcapacitor assembly as a function of copolymer type and concentration. Our robust and simple procedure to tune the MWNT microcapacitor network in polymer blends via the efficiency of the compatibilizer can be used to achieve a synergistic increase in the dielectric properties

at different length scales.

Keywords:

Polymer blend, phase separation, carbon nanotubes, compatibilization, interfacial capacitance, microcapacitor, dielectric properties.

1. Introduction

When developing immiscible polymer blends with enhanced properties, block¹ and random copolymers² play an essential role in refining and stabilizing the biphasic morphology. The copolymers architecture³ and molecular weight⁴ govern its interfacial activity and its resulting efficiency in compatibilizing the blend morphology. The copolymers physical characteristics affect morphology refinement differently under flow and quiescent conditions encountered respectively during melt mixing and thermal annealing of immiscible blends.⁵ In phase separating blends, the extent of symmetry of the copolymers strongly affects the miscibility range,⁶ which further alters the quench depth and the phase separation kinetics. In addition, both the copolymer type and its molecular weight govern its ability to reach the interface and to stabilize the biphasic morphology against coarsening.⁷ Copolymers with various physical characteristics can thus be used to create blend systems with a wide range of morphologies at the same blend composition. Varying the compatibilizers efficiency can be used to tailor the blend morphology and to improve the resulting blend properties. The consequences of an effective compatibilization for the physical properties of biphasic blends such as mechanical or dielectric behavior have been studied. For example, the mechanical properties of immiscible blends can be significantly enhanced upon compatibilization due to improved adhesion of the blend components,⁸ with the efficiency being correlated with the compatibilizers composition⁹ and architecture.³ Long random copolymers can be more effective than long symmetric diblock

copolymers in reinforcing interfaces.² This has been attributed to the ability of the long
 random copolymers to have multiple crossings at the interface, forming loops which entangle
 with the homopolymers and, thereby, effectively stitch the two immiscible homopolymers
 together.² Recently, it was shown that an increase in the molar mass of the PMMA end
 blocks in PMMA-PE-PMMA triblock copolymers results in an increase of the mechanical
 properties of PE-PMMA blends, which was attributed to an enhanced entanglement
 density and increased interfacial width at the PE/PMMA interface.¹⁰ Similarly, maximum
 fracture toughness of the interface between the components of an immiscible PS-PMMA
 blend resulted from a symmetrical interfacial broadening due to PS-r-PMMA.¹¹ From the
 perspective of blends dielectric properties, differences in the dielectric and/or conducting
 properties of the blend components further lead to interfacial blocking of charge carriers.¹²
 An understanding of the consequences of effective compatibilization for the interfacial
 dynamics and the associated length scales would allow to develop polymeric materials
 with enhanced dielectric properties. Recently, we have studied the effect of an interfacially
 segregated PS-r-PMMA random copolymer on the interfacial dynamics of a phase separated
 blend of P α MSAN and PMMA.¹³ The interfacially segregated compatibilizer simultaneously
 affected the blocking of charge carriers at the interface and refined the dispersed phase in
 which the charge entrapment occurred. The complex interplay of the respective length
 scales determined the final blend dielectric properties.¹³
 In blends with selectively localized conductive nanoparticles, compatibilizers can also
 enhance the blend conductivity as a consequence of their effect on the blend morphology.^{7,14}
 For example, in phase separating P α MSAN/PMMA blends with MWNTs, an interfacially
 segregated long random copolymer was used to steer the formation of a percolated network
 of MWNTs in the P α MSAN phase, which resulted in an increase of the blend conductivity
 by 4 decades with 0.5 wt% MWNTs upon addition of only 0.25 wt% copolymer.¹⁵ We
 recently demonstrated that varying the copolymers architecture (block or random) and
 molecular weight can be used to tune the phase separated blend morphology and corre-

sponding conductivity.⁷ In polymer nanocomposites with conductive particles, not only the conductivity, but also the dielectric properties have been studied to some extent. Polymer nanocomposites with high dielectric permittivity provide an ideal solution to combine the dielectric and conducting properties of the ceramic or metal fillers and the mechanical properties of the polymer matrix. As a result, these dielectric materials find tremendous application in electromechanical devices, supports of electronic circuits, cable accessories in electrical engineering and in many civilian and military applications.¹⁶ Specifically dielectric polymer materials are embedded into the inner layers of organic printed circuit boards (PCB) because of their flexibility and good compatibility with the PCB material, for which it is essential for the composites to exhibit a low percolation threshold.¹⁷ In this context, the present work aims to improve the dielectric properties of MWNT filled polymer blends at a low MWNT concentration.

Nearby conductive particles enclosing a layer of dielectric polymer form a microcapacitor, with the particles forming the capacitor electrodes. These microcapacitor configurations are not perfect capacitors but can be modeled as a resistor and capacitor in parallel.¹⁸ Such microcapacitors can provide extremely high dielectric permittivities to the materials.¹⁹ For rubber composites with MWNTs, the relaxation process of the MWNT/MWNT connections exhibits the characteristics of a tunneling process. Using this framework, the resistivity and gap distance of the microcapacitors was calculated from the dielectric properties. A pronounced decrease in both the resistivity and gap distance of the microcapacitor was obtained with increasing MWNT concentration.¹⁸ Furthermore, the interfacial polarization of MWNTs in a polyvinyl alcohol composite was modeled using an equivalent circuit consisting of resistor-capacitor elements in series allowing to decouple the bulk behavior from that of the electrode-sample interface.²⁰ At present, the effect of a microcapacitor network in one of the blend phases on the blend dielectric properties and the effect of the morphology on the latter is unknown. The goal of our research is to address the consequence of compatibilization of the blend on the microcapacitor network formed by

entrapped P α MSAN between adjacent MWNTs at the same MWNT concentration. The interfacial properties along with the mechanism of charge transfer of the MWNTs through the entrapped P α MSAN will be studied. This will allow to elucidate the effect of various copolymers on the physical parameters governing the dielectric properties of the blends and their length scales. A systematic understanding of the filler-filler, filler-matrix polymer and filler-entrapped polymer-filler interactions and their associated length scales will allow to tailor physical properties of the blends by an effective compatibilization. Our findings will be pivotal for developing a rational design of cost-effective high performance biphasic polymer blends with improved dielectric properties.

2. Experimental Section

2.1. Materials

The homopolymers poly[(α -methyl styrene)-co-acrylonitrile] (P α MSAN) (Luran KR2556) and poly(methyl methacrylate) (PMMA) (Lucryl G77) were purchased from BASF. The P α MSAN-PMMA blend is miscible at low temperatures and phase separates by spinodal decomposition upon heating above the lower critical solution temperature (LCST) at 165 °C for blends containing 40 wt% P α MSAN.²¹ Amine functionalized multiwall carbon nanotubes (MWNTs) were purchased from Nanocyl (NC3152). It is well-known that these MWNTs selectively localize in the P α MSAN phase, which is their thermodynamically preferred phase.^{7,15,22} The phase separated morphology is compatibilized by either random or block poly(styrene)-poly(methyl methacrylate) (PS-PMMA) copolymers with various molecular weights. The physical characteristics of the blend components and copolymers chosen in the study are compiled in Table 1. The set of copolymers has been chosen to cover a wide range of compatibilization efficiencies, corresponding to different levels of interfacial activity, as shown by Bharati et al.⁷

Table 1. Physical characteristics of the blend components and copolymers.

Component	Company	M_w (kg/mol)	M_w/M_n	Composition (M_w (kg/mol))
PαMSAN	BASF (Luran KR2556)	82.0	2.4	70% PαMS 30% PAN
PMMA	BASF	88.0	2.1	95% PMMA, 5% PMA
PS-r-PMMA	Polymer Source	33.8	1.3	$M_w^{PS} = 13.5$, $\frac{M_w^{PMMA}}{M_w^{PS}} = 1.5$
PS-r-PMMA	Polymer Source	192.0	1.6	$M_w^{PS} = 61.5$, $\frac{M_w^{PMMA}}{M_w^{PS}} = 2.1$
PS-r-PMMA	Polysciences	270.0	5.0	$M_w^{PS} = 189.0$, $\frac{M_w^{PMMA}}{M_w^{PS}} = 0.4$
PS-b-PMMA	Polymer Source	36.8	1.18	$M_w^{PS} = 18.4$, $\frac{M_w^{PMMA}}{M_w^{PS}} = 1.0$
PS-b-PMMA	Polymer Source	291.0	1.18	$M_w^{PS} = 145.5$, $\frac{M_w^{PMMA}}{M_w^{PS}} = 1.0$

2.2. Blend processing

One-step melt mixing was used to prepare 40/60 (wt%/wt%) PαMSAN/PMMA blends with or without 0.5 wt% MWNTs and 0, 0.25, 0.5 and 2 wt% PS-PMMA copolymers. A 15 cm³ DSM microcompounder with a rotational speed of 60 rpm for 20 min was used under inert nitrogen conditions at 200 °C. PαMSAN nanocomposites with a concentration of MWNTs (1.25 wt%) equivalent to that in the blends taking into account the selective localization in the PαMSAN, were extruded under similar conditions. Due to the torque limitations of the mini-extruder, the blend processing was performed at a temperature (200 °C) above the LCST of the 40/60 PαMSAN/PMMA blend (165 °C), resulting in phase separated blends. Subsequently, these blends were compression molded below the LCST (at 160 °C) for 8 min under 50 MPa using a laboratory press (Collin). This resulted in monophasic blends, as verified by Bose et al.²² using DMTA. Phase separation of the compression molded samples (25 mm diameter and 1.5 mm thickness) was performed under nitrogen atmosphere at 220 °C in a rheo-dielectric setup for 5 hrs. After this time, both the elastic moduli as well as the conductivity had reached steady state values.

2.3. Characterizations

The dielectric measurements were performed with a rheo-dielectric setup by employing a Novocontrol Alpha analyzer in combination with an MCR501 stress controlled rheometer (Anton Paar). Measurements were performed on the phase separated samples (25 mm diameter and 1.5 mm thickness), placed in between the parallel plates of the rheometer, which acted as electrodes for dielectric measurements. Dielectric spectroscopy measurements were conducted in the frequency range of 10^{-2} to 10^7 Hz. High temperatures were maintained with a CTD450 temperature controlled convection oven under nitrogen atmosphere. Temperatures below as well as above the phase separation temperature were used. For temperatures below the phase separation temperature, measurements were performed above the components glass transition temperature (T_g), which allowed good electrical contact. The dielectric scans at each temperature were performed on different samples and the absence of remixing was verified by DSC.¹³ The data were analyzed by calculating the dielectric permittivity and the real part of the conductivity from the complex impedance values and the sample dimensions.^{12,23} The contribution of conductivity to the dielectric loss (ϵ'') was eliminated by calculating ϵ'' from the dielectric constant (ϵ') using $d\epsilon'/d\ln f$ as an approximation of the Kramers-Kronig (KK) transformation.²³ The Nyquist impedance spectra were fitted with an appropriate equivalent circuit using ZVIEW2 software to simulate the experimental impedance response.

3. Results and discussion

3.1. MWNT-P α MSAN Interfacial Capacitance

3.1.1. Characterization of the Dynamics and Origin of the Interfacial Peak

In our recent work, we elucidated the effects of copolymer architecture and molecular weight in improving the connectivity and refinement of the P α MSAN phase with MWNTs in phase separated P α MSAN-PMMA blends.¹⁵ In the present work, we will probe the interfacial dynamics of the blends with MWNTs and copolymer to evaluate the effects of an improved microstructure on the interfacial dielectric properties. Interfacial dielectric relaxations arise due to a contrast in electrical permittivity and/or conductivity of the different constituents.^{12,24} The interfacial dynamics in blends with MWNTs and rcp may involve the cumulative effect of the polarization of various interfaces, namely that of the more conducting P α MSAN with the less conducting rcp and that of the selectively localized conducting MWNTs with enclosed dielectric P α MSAN chains. Here, we will first attempt to identify the presence and origin of such an interfacial peak in compatibilized blends with selectively localized MWNTs. Thereto, the interfacial relaxations in the compatibilized biphasic P α MSAN-PMMA blends with MWNTs will be compared with the dynamics of the P α MSAN at the rcp interface in the neat biphasic blend (without MWNTs) as well as that of the conducting MWNTs with the entrapped dielectric P α MSAN chains in a P α MSAN composite having an equivalent concentration of MWNTs (1.25 wt% MWNTs) as in the blends (0.5 wt% MWNTs in 40 wt% P α MSAN).

The “conduction free” dielectric relaxation spectra of the homopolymers and biphasic blends with 0.5 wt% rcp of 270 kg/mol with and without 0.5 wt% MWNTs near the constituents T_g (130 °C) are shown in Figure 1a and b, respectively. The conductivity contributions originating from the blend components above their T_g as well as from the MWNT network were removed for blends without and with MWNTs. The dielectric spectra of the blend components as well as P α MSAN/PMMA blends with and without copolymer have been de-

scribed in detail elsewhere¹³ and will only be discussed briefly here. In the “conduction free” dielectric relaxation spectra of the homopolymers in Figure 1a, a high frequency (10 kHz - 1 MHz) β relaxation is observed in the homopolymers, which also appears in the blends and composites (Figure 1b). The stronger β relaxation in PMMA is attributed to the coordinated rotation of the $-\text{COOCH}_3$ side groups around the backbone chain of PMMA.^{25,26} At intermediate frequencies (1 Hz - 10 kHz), a segmental (α) relaxation is discerned in the homopolymers, and its contribution in the blends (Figure 1b) is owed to both the blend components. Considering the higher dielectric strength and slower dynamics of the α relaxation in P α MSAN as compared to that of PMMA due to the stronger cooperative motions of the backbone chain of P α MSAN, we believe the α relaxations of P α MSAN are primarily manifested in the blends and composites. At low frequency (below 1 Hz) an increase in the “conduction free” dielectric relaxation spectra is observed in biphasic blends with and without MWNTs, which has a higher dielectric strength and slower relaxation as compared to the segmental and molecular relaxations in Figure 1a. Such a strong low frequency relaxation peak is typically of interfacial origin.¹³

At low frequencies, the “conduction free” dielectric relaxation spectra of the homopolymers in Figure 1a also increase with decreasing frequency (with a slope less than 1) due to weak electrode polarization effects. For the blends and composites the low frequency relaxation peak is more pronounced. Moreover, it was unaffected by performing measurements at a reduced sample thickness of $\approx 400 \mu\text{m}$ (as compared to 1.5 mm), which is uncharacteristic of electrode polarization.²³ Hence, the low frequency relaxation in the blend without the MWNTs is of an interfacial origin and results from the entrapment of occluded P α MSAN charges ($\sigma_{dc} \approx 10^{-13} \text{ S/cm}$ at 130 °C) at the interface with less conducting interfacially segregated copolymer ($\sigma_{dc} \approx 10^{-15} \text{ S/cm}$ at 130 °C). Moreover, with increasing concentration of the copolymer, an increase of the dielectric strength of the interfacial polarization was observed, resulting from a decrease of the Debye length.¹³ In summary, a low frequency and high temperature dielectric relaxation peak of interfacial origin is observed in the biphasic

Figure 1. Comparison of “conduction free” dielectric loss spectra of (a) homopolymers PMMA and P α MSAN, (b) biphasic 40/60/0.5 P α MSAN/PMMA/rcp 270 kg/mol blends with and without 0.5 wt% MWNTs, and P α MSAN composite with 1.25 wt% MWNTs above the T_g of the homopolymers (130 °C). The indicated peaks are assigned to their respective contributions. $\alpha_{interface}$ originates from the polymer-polymer interface, whereas $\alpha'_{interface}$ originates from the MWNT-polymer interface.

blend without MWNTs due to a conductivity contrast of 2 decades between the dispersed 1
polar P α MSAN and the interfacially segregated copolymer. 2

Upon addition of 0.5 wt% MWNTs, the biphasic blend with 0.5 wt% rcp also reveals a 3

low frequency polarization peak in Figure 1b. However, its dielectric strength is two decades larger than the strength of the interfacial polarization in the biphasic blend without MWNTs. Since it is established that the dielectric strength in these blends increases more or less proportional with the intrinsic length scale of the biphasic blend, i.e. the ratio of structure dimension (D_v) to Debye length (L_D),¹³ we cannot attribute the two decades increase of the dielectric strength to the marginal refinement effects achieved from the 0.5 wt% MWNTs.⁷ As the MWNTs are preferentially segregated only in the P α MSAN phase, the possibility of probing the interface between the MWNTs and entrapped P α MSAN cannot be ruled out. Therefore, the loss spectrum of a P α MSAN nanocomposite with an equivalent concentration of MWNTs as in the blend (1.25 wt% MWNTs) has been included in Figure 1b to study the dynamics of the interface of entrapped P α MSAN chains between neighboring MWNTs. Interestingly, a stark resemblance of the dielectric strength of the interfacial polarization of MWNTs-P α MSAN in the composite and in the blend offers substantial support to the fact that we are probing the same interface in the biphasic blend with MWNTs. As the P α MSAN composite with 1.25 wt% MWNTs is inherently not percolating,²⁷ the presence of electrode polarization in the composite at low frequencies can be ruled out, which was also verified by the unchanged dielectric strength of the low frequency relaxation at a sample thickness of 400 μ m as compared to 1.5 mm. In conclusion, a substantial increase of the dielectric relaxation strength by over 2 decades in magnitude at low frequencies is observed for biphasic blends with 0.5 wt% rc upon addition of 0.5 wt% MWNTs, whose origin is attributed to the polarization of the MWNTs charges at the interface with entrapped P α MSAN chains. To further verify the origin of the dielectric interfacial polarization at low frequencies, its dynamics in the studied composites and blends is investigated as a function of temperature in Figure 2. Thereto, the dielectric interfacial relaxation peak was fitted using the Havriliak Negami (HN) function:²⁸

$$\epsilon''(\omega) = Im(\sum \frac{\Delta\epsilon}{[1+(\omega\tau_{HN})^a]^b})$$

$$\Delta\epsilon = \epsilon_s - \epsilon_\infty$$
(1)

where ϵ_∞ is the dielectric constant at limiting high frequencies, τ_{HN} is the characteristic relaxation time, and a and b are the shape parameters, characteristic of the width and peak asymmetry of the relaxation time distribution function, respectively. The dielectric strength and relaxation time of the interfacial polarization obtained using the HN function for temperatures above the T_g of the homopolymers (130 °C) and below the phase separation temperature of the blend (160 °C) are plotted in Figure 2. The interfacial relaxation time shows a slight deviation from a linear temperature dependence, and hence has been fitted using the Vogel-Fulcher-Tammann (VFT) function²⁹⁻³¹ (lines in Figure 2):

$$\tau_{max} = \tau_\infty \exp \frac{E_v}{R(T-T_v)} \quad (2)$$

where τ_∞ is the pre-exponential factor and corresponds to the relaxation time at the limit of infinite temperature, R is the universal gas constant, E_v is the “Vogel activation energy” in kJ/mol and T_v is the Vogel temperature, below which the system is frozen and relaxation is absent. This non-linear temperature dependence of the interfacial relaxation time points to a spatial gradient of the properties of entrapped P α MSAN chains between adjacent MWNTs.

Upon comparison of the temperature dependence of the interfacial relaxation times in the blends and composites in Figure 2, it can be concluded that the difference in the temperature dependence of the interfacial relaxation time in the three systems is insignificant. Imperatively, a close agreement between the relaxation strength of the biphasic blend with MWNTs and that of the P α MSAN nanocomposite with an equivalent concentration of MWNTs is observed for the entire temperature window. In summary, a striking similarity of the dielectric interfacial strength and relaxation time of the MWNTs-P α MSAN interface both in the blends and the composites over the entire temperature window corroborates our finding that we are studying the dynamics of the MWNTs-P α MSAN interface in the biphasic compatibilized blend at low frequencies. In the ensuing sections, we will estimate the capacitance of the dielectric interfacial relaxations of the MWNTs-P α MSAN network and will further

Figure 2. Temperature dependence of the dielectric strength $\Delta\epsilon$ (left) and relaxation time (right) determined from the Havriliak Negami (HN) function for interfacial polarization of biphasic 40/60/0.5 P α MSAN/PMMA/rcp 270 kg/mol blends with and without 0.5 wt% MWNTs and P α MSAN composite with 1.25 wt% MWNTs.

investigate the effect of various copolymers on the estimated capacitance.

3.1.2. Determination of Interfacial Capacitance by means of Impedance Spectroscopy

The dynamic response of the biphasic blend may allow to quantify the effect of copolymer on properties at different length scales. In this regard, we demonstrated the ability of an effective compatibilizer to tailor a percolated network of selectively localized MWNTs and to augment the resulting conductivity.⁷ The study in this section will shed light on the local morphology and the associated dynamics, based on the interfacial capacitance pertaining to the MWNTs-P α MSAN interface in blends with various copolymers. To shift the interfacial peak fully into the measurement frequency window to further increase the accuracy of the analysis, we study the interfacial polarization effects in the AC conductivity spectrum at 220

°C. Thus, to identify the various polarization effects in the biphasic blends, the steady state AC conductivity spectrum for the blend with 0.5 wt% MWNTs and 0.25 wt% rcp of 270 kg/mol at 220 °C is presented in Figure 3a as a representative example. The AC conductivity spectra of the blend components as well as PαMSAN/PMMA blends containing 0.5 wt% MWNTs with and without 270 kg/mol rcp at 220 °C have been discussed elsewhere.¹⁵ To deconvolute the various contributions to the conductivity spectrum of biphasic blends with 0.5 wt% MWNTs and 0.25 wt% rcp of 270 kg/mol, we have used the following empirical equation describing the universal AC behavior of a percolated system to model the conductivity response of the blends:³²

$$\sigma'(\omega) = \sigma_{DC} + \frac{\omega\epsilon_0\Delta\epsilon(\omega\tau)^a \sin(\pi/2)}{1+2(\omega\tau)^a \cos(\pi/2)+(\omega\tau)^{2a}} + B\omega^s \quad (3)$$

where σ_{dc} is the low frequency plateau of AC conductivity, ω is the angular frequency, $\Delta\epsilon$ is the dielectric strength of interfacial polarization, τ is the characteristic relaxation time, a is the shape parameter characteristic of the dispersion of the peak, B is a temperature dependent parameter and the exponent s is temperature dependent and varies between 0 and 1. In eq 3, the first term for frequency independent conductivity is a measure of the long range connectivity of the MWNTs. The second term predicts the conductivity peak from the interface of entrapped PαMSAN between adjacent MWNTs, which occurs at intermediate frequencies. The dielectric interfacial relaxation was verified to be symmetric using the HN function.²⁸ In other words, the parameter characterizing the asymmetric behavior of the relaxation, b in eq 1 is equal to 1, and we have used a Cole-Cole distribution (second term in eq 3) to predict the interfacial conductivity response of the biphasic blends. The third power law term occurring at high frequencies describes the frequency behavior of electron conduction in disordered materials (MWNTs). In Figure 3a, above 1MHz, the short-time dynamics is characteristic of hopping of MWNTs charges to a nearby spatially separated localized state in which the MWNTs charges sub-diffuse through the barrier imposed by

their structural disorder.³³ This leads to a dispersive conductivity at high frequencies, which increases with frequency with a power law exponent 's' ≈ 0.8 . The Dyre model³⁴ for percolation conduction of electron-conducting disordered materials predicts s between 0.7 and 1 for hopping of charge carriers over spatially random barriers. The estimated s falls in the range of hopping transport between the MWNTs,³² which is schematically depicted in Figure 3a. Schematics of the morphology for the various contributions to the conductivity spectrum are shown in Figure 3a and the cumulative result of the fitting using eq 3 is shown as a bold line in Figure 3a.

The conductivity spectrum in Figure 3a shows the presence of an interfacial polarization at intermediate frequencies, which is the same polarization as that in Figure 1b, but shifted to higher frequencies due to the increased temperature. We will employ the permittivity spectrum to obtain further insight in the various polarizations in the studied blend system, which we believe may be linked to the connectivity at various length scales, corresponding to the 3 regions indicated in Figure 3a. Thereto, the permittivity spectrum of a biphasic blend containing 0.5 wt% MWNTs and 0.25 wt% rcp of 270 kg/mol at 220 °C is shown in Figure 3b. The ϵ' above 1MHz is frequency independent in Figure 3b. This is due to the fact that the structural (α) and molecular (β) relaxations of the components are outside the measuring frequency window as the probed temperature of 220 °C is well above the constituents T_g (≈ 100 °C). This corresponds to the region of MWNT-MWNT electron hopping in the conductivity spectrum. From few kHz to 1MHz, a Cole-Cole distribution for the interfacial polarization in the conductivity response (Figure 3a) manifested in a step increase in ϵ' and a corresponding Debye-like relaxation peak in ϵ'' in Figure 3b. A pronounced increase in ϵ' and $\epsilon''_{conduction\ free}$ is obtained below 10Hz owing to the contribution from electrode polarization. As the slope of $\epsilon''_{conduction\ free}$ is slightly less than 1 for electrode polarization, with decreasing frequency, σ' slightly decreases (using $\sigma' = \omega\epsilon_0\epsilon''$) from the dc plateau owing to the contribution of the conductivity through the imperfectly blocking double layer at the electrodes. Nevertheless, the conductivity of the percolated MWNT network dominates the

Figure 3. (a) Steady state AC conductivity spectrum at 220 °C for biphasic 40/60 PαMSAN/PMMA blends with 0.5 wt% MWNTs and 0.25 wt% rcp of 270 kg/mol. The fitted data (eq 3) is shown as red bold line. The contributions obtained from DC conductivity (term 1 in eq 3), interfacial polarization (term 2 in eq 3) and power law (term 3 in eq 3) have been demarcated. Inset: Schematic of the morphology for the various contributions of the conductivity spectrum, where MWNTs are represented by black solid lines. (b) Dielectric permittivity and “conduction free” dielectric loss spectrum at 220 °C of the biphasic blend whose steady state AC conductivity spectrum is shown in (a). The contributions from electrode polarization, entrapped PαMSAN-MWNT interfacial polarization and MWNT-MWNT polarization have been demarcated.

DC conductivity as compared to the conductivity at the electrodes in Figure 3a. It should be noted that the interfacial polarization in the PαMSAN/PMMA blends without MWNTs

occurs at a frequency around 1 kHz (data not shown) at this temperature. Due to its low dielectric strength with respect to that of the P α MSAN/MWNT interface, it does not show up in the blends with MWNTs. In conclusion, we successfully de-convoluted the dynamic response of the conductivity and permittivity spectrum of the blend.

Having elucidated the various polarization contributions, the task of deconvoluting and estimating the capacitance from the various polarizations is performed by using the impedance response of the studied biphasic blend system. The equation that relates the impedance (Z^*) with the dielectric properties is given by:¹²

$$\epsilon^*(\omega) = \frac{1}{i\omega Z^*(\omega)C_0} \quad (4)$$

Henceforth, the Nyquist impedance spectrum corresponding to the permittivity spectrum presented in Figure 3b is shown in Figure 4a. The various polarizations manifest themselves as semi-circular arcs, whose contributions as discussed in Figure 3a, b have been assigned in Figure 4a. It can be seen from Figure 4a that the Nyquist impedance spectrum is dominated by the response of the interface, which makes it an excellent tool to study this process. To quantify the physical processes in the blend whose dynamics is originating from local length scales, interface and surface effects, it is imperative to design an electrical circuit model which mimics the response of the current through a path offering the least resistance to the various polarizations.³⁵ The equivalent circuit model treats a dynamic process as a random mixture of resistors and capacitors. Subsequently, these elements should be correlated with the physical state of the various processes which the system undergoes, as shown in Figure 3a. At high frequencies, the electronic charge carriers of the MWNTs scan distances between the MWNTs, whose polarization is simulated using a parallel combination of R_{MWNT} and C_{MWNT} . Furthermore, the entrapment of charge at the MWNT-P α MSAN interface with disparate properties is accounted for by another RC element. However, instead of an ideal capacitor, a constant phase element ($CPE_{interface}$)

Figure 4. (a) Corresponding Nyquist impedance spectrum of the blend whose conductivity and permittivity spectra are shown in Figure 3a and b, respectively. The fitted data is shown as red line using the (b) equivalent circuit consisting of a RC and 2 RQ elements in series, where CPE in the RQ element stands for constant phase element.

has been chosen to take into account the spatial gradient of the properties at the interface. 1
The resistance offered by the imperfect blocking of charges at the MWNT-PαMSAN 2
interface is captured by $R_{interface}$, which forms a parallel pathway with $CPE_{interface}$. 3
The impedance of the CPE is represented by $Z_{CPE}^* = 1/(Q\omega^\alpha)$, where Q takes into account 4
the interfacial capacitance ($C_{interface}$) and α denotes the frequency dependence of the 5
capacitive behavior.³⁵ For a parallel combination of a resistor and a CPE, the $C_{interface}$ 6
can be calculated from Q using $C_{interface} = Q\omega_{max}^{\alpha-1}$, where ω_{max} is the frequency at which 7
 Z'' attains a maximum.³⁶ Furthermore, the resistance owing to the leakage of charges at 8
the blocking electrodes ($R_{electrode}$) forms a parallel network with the imperfect double-layer 9
capacitance ($CPE_{electrode}$) at the electrodes. Hence, in conclusion, the impedance response 10

of the blend was simulated with a series combination of 2 parallel RQ elements and a parallel RC element and the result is shown in bold lines in Figure 4a. The values of the R_{MWNT} between MWNTs for 0.5 wt% concentration (≈ 10 kOhms) obtained from fitting is of the same order of magnitude as the contact resistance for MWNTs undergoing hopping charge transport when embedded in vulcanized silicone rubber.³⁷ A low contact resistance between the MWNTs as obtained in this study is encountered in carbon nanotubes when their electronic states are coupled,³⁸ and even between two metals with good contact.³⁹ We thus successfully simulated the experimental impedance response for all blends using our developed equivalent circuit model. The physical state of the probed interface at the mesoscopic length scales will be deduced in the next section via the interfacial capacitance.

3.1.3. Effect of Copolymers on the Interfacial Capacitance and Resistance

In this section, the effects of rcp and bcp molecular weight and concentration on the storage ability of the MWNT charges by the entrapped P α MSAN between the adjacent MWNTs will be investigated, and will subsequently be linked to the connectivity of the entrapped polymer - MWNTs. The charge storage is quantified by the interfacial capacitance ($C_{interface}$), which was estimated from the equivalent circuit (Figure 4b) fitting of the Nyquist impedance spectrum (Figure 4a). Thus, the calculated interfacial capacitance is presented in Figure 5 for blends with increasing molecular weights and copolymer concentration of rcp and bcp. For both rcp cases having a copolymer M_w less than the homopolymers M_w (rcp 34 and rcp 192), a sluggish increase in $C_{interface}$ by a decade and saturation is observed with increasing copolymer concentration. However, a significant increase in $C_{interface}$ by several decades is observed for blends with only 0.25 wt% copolymer irrespective of the M_w of the blocks in the case of bcp and for rcp long enough to entangle with the homopolymers. In this regard, bcp of all M_w 's and long rcp improved the connectivity and refinement of the P α MSAN domains containing MWNTs.⁷ This suggests that the compatibilization of the microstructure resulted

Figure 5. Interfacial capacitance of the MWNTs-entrapped P α MSAN network obtained from Figure 4a, b versus rcp and bcp concentration for biphasic 40/60 P α MSAN/PMMA blends with 0.5 wt% MWNTs at 220 °C. The number in the copolymer name indicates its molecular weight (kg/mol).

in an increase in the interfacial capacitance of the MWNTs with entrapped P α MSAN. The trends in $C_{interface}$ for blends with various rcp/bcp are qualitatively the same as that for the electrical conductivity achieved upon increasing the long-range connectivity of the MWNT network selectively localized in the P α MSAN phase.⁷ Moreover, the observed increase and saturation behavior of the interfacial capacitance corresponds to a simultaneous drop and saturation of the interfacial resistance ($R_{interface}$) of the probed interface with effective compatibilization (Figure 6). In summary, effective compatibilization leads to a pronounced increase in the charge storage capacity ($C_{interface}$) of the interface formed by entrapped P α MSAN between adjacent MWNTs.

The physical state and connectivity of the MWNT-P α MSAN interfaces exhibiting a pronounced increase in $C_{interface}$ with increasing copolymer concentration and M_w can be understood in terms of charge carrier diffusion in the resistor - capacitor network of entrapped

Figure 6. Interfacial resistance of the MWNTs-entrapped P α MSAN network obtained from Figure 4a, b versus rcp and bcp concentration for biphasic 40/60 P α MSAN/PMMA blends with 0.5 wt% MWNTs at 220 °C. The number in the copolymer name indicates its molecular weight (kg/mol).

P α MSAN - MWNTs. Presence of strong polymer-filler interactions leads to entrapment of the polymer chains, in which the thickness of bound polymers determines the mode and dynamics of the charge carriers between the fillers.⁴⁰ In the framework of the microcapacitor model, two neighboring MWNTs form two electrodes enclosing a thin layer of dielectric material, and a network of these local capacitors expands between the imposed electrodes.⁴¹ Due to the resistive contribution of the entrapped P α MSAN chains to the transport of electronic charge carriers between the adjacent MWNTs, the biphasic blends do not exhibit the intrinsic conductivity ($\approx$ few S/cm) of MWNTs. An increase in the static permittivity (normalized $C_{interface}$) with increasing filler concentration until the percolation threshold, followed by saturation above the percolation threshold of the filler was reported for Polycarbonate (PC)-MWNT composites.⁴² The behavior was attributed to the formation of microcapacitors

at the gaps (and possibly free ends) between the MWNTs and the bound polymer. In our framework, increasing the continuity of the MWNT-containing P α MSAN phase by means of copolymers leads to the formation of an extended continuous network of microcapacitors. In summary, the pronounced effect of increased connectivity of MWNT-entrapped P α MSAN on its capacitive properties was successfully demonstrated in this section.

3.2. Gap spacing of the MWNT-P α MSAN microcapacitor

The physical state of the entrapped polymer between the fillers dictates the stress transfer by the filler network, and the characteristic gaps between the MWNTs engender a barrier for the transportation of charge through the entire filler network.⁴³ Hence, the physical state and characteristic gaps of the probed MWNT-P α MSAN elements in our biphasic blend system are relevant for the properties and can be probed via the interfacial relaxation. An estimation of the characteristic gap of the microcapacitors can be made from the interfacial resistance and capacitance when knowing the mechanism of conductivity in the MWNT-P α MSAN elements forming the microcapacitors. The presence of the dielectric P α MSAN between neighboring conducting MWNTs results in a potential barrier to inter-nanotube hopping. This can result in a different conduction mechanism, whose barrier and temperature dependence of conductivity could be different from that for hopping of MWNT charge carriers. Based on the fact that percolating P α MSAN nanocomposites and biphasic blends with MWNTs do not exhibit the intrinsic conductivity of MWNTs ($\approx$ few S/cm), we surmise that the electron transport through the P α MSAN between adjacent MWNTs is controlled by fluctuation induced tunneling, as reported by Kilbride et al.⁴⁴ for PmPV and PVA based carbon nanotube composites and Fritzsche et al.⁴³ for carbon black-SB rubber composites. Since the temperature dependence of the conductivity contains intrinsic information about the imposed barrier to electron transfer and the mechanism of conductivity, the logarithm of the DC conductivity of the MWNT-P α MSAN nanocomposite having equivalent concentration of MWNTs (1.25 wt%) as in the blend (0.5 wt%) was plotted versus the reciprocal of the

absolute temperature. A strong linear dependence was obtained indicative of the presence of thermal fluctuation induced tunneling (FIT).^{17,45} The activation energy of the thermally activated FIT process was calculated by expressing the FIT model ($\sigma = \sigma_0 \exp[-T_1/(T+T_0)]$)⁴⁶ in the form of a VFT equation (eq 2) for conductivity ($\sigma = \sigma_0 \exp[E_v/R(T-T_v)]$)^{29,30}. Here, σ_0 is the pre-exponential factor, T_1 is the energy barrier imposed for the electron to tunnel the insulating barrier and is analogous to the Vogel activation energy (E_v), R is the universal gas constant and T_0 is an estimate of the lowest temperature above which tunneling is thermally active corresponding to the Vogel temperature T_v . Thus, the activation energy was estimated to be ≈ 0.9 eV from the slope of the temperature dependence of the DC conductivity. The predicted activation energy is in reasonable agreement with the values obtained for tunneling of carbon black charges across barriers of polyvinylchloride⁴⁶ and for the conductivity owing to tunneling of MWNT electrons through the barriers imposed by the adsorbed PVDF near and above the T_g of PVDF.¹⁷ In this respect, the fitting parameters and the activation energy obtained from the FIT model depend on the interaction of the polymer matrix and the filler, the aspect ratio and the concentration of the filler.⁴⁷ In summary, at high frequencies the electrons hop between the neighboring MWNTs, whereas at intermediate frequencies, the electrons of MWNTs tunnel through the barriers imposed by the entrapped P α MSAN.

The interfacial relaxation process is attributed to the transfer of electrons of MWNTs by tunneling through the gap occupied by the entrapped polymer between the adjacent MWNTs. In this respect, the gap between the adjacent filler particles determines the barrier, and hence, the interfacial resistance and capacitance between the adjacent fillers. In the case of fluctuation induced tunneling, the capacitance shows the typical inverse relationship with the gap width δ whereas the model predicts an exponential growth of the interfacial resistance with increasing gap between the MWNTs, given by:⁴⁸

$$C_{interface} = \epsilon_0 \epsilon \frac{A}{\delta} \quad (5)$$

$$R_{interface} = \frac{16\pi^2\hbar}{3e^2} \frac{\delta}{k_0 A} \exp(k_0\delta) \quad (6)$$

$$k_0 = \frac{2\sqrt{2m_e}}{\hbar} \sqrt{V} \quad (7)$$

where A is the cross section of the capacitor, e the electronic charge, m_e the mass of an electron, $\hbar$ the Planck's constant and k_0 depends on the height of the potential barrier V . The combined effects of the capacitor width as well as area in eqs. 5 - 7 complicate determination of any of these parameters from $R_{interface}$ and $C_{interface}$. However, from the relaxation time for the tunneling process ($\tau_{interface}$) obtained by combining $R_{interface}$ and $C_{interface}$, the gap spacing can be obtained:⁴³

$$1/\tau_{interface} = 1/R_{interface}C_{interface} = \frac{3e^2}{16\pi^2\hbar} \frac{k_0}{\epsilon} \exp(-k_0\delta) \quad (8)$$

As an alternative to the combination of $R_{interface}$ and $C_{interface}$, $\tau_{interface}$ can also be obtained directly from the HN fitting of the interfacial relaxation in the “conduction free” dielectric loss spectra (Figure 3b). Both approaches exhibited a remarkable agreement, which serves as an indirect proof of the accuracy of the estimated $R_{interface}$ and $C_{interface}$ values from Figure 4a.

As the capacitance scales inversely with the thickness of the insulator region (eq 5),¹² a smaller gap would lead to a decrease in the contact resistance and an increase in the interfacial capacitance. The dielectric constant of P α MSAN in the capacitor for estimating the gaps in eq 8 was taken to be 3.1. For a potential barrier of 0.5 eV, characteristic for MWNTs,^{18,33} the gap of the capacitor was found to be ≈ 21 nm for blends with only 0.5 wt% MWNTs. Furthermore, the gap spacing was estimated to be 15 - 18 nm for blends with 0.5 wt% MWNTs and with increasing concentrations of various rcp and bcp. The invariant gap spacing with copolymer architecture and concentration is expected as we have proven via rheology and conductivity measurements that the copolymer does not affect the dispersion of the MWNTs in P α MSAN-MWNT nanocomposites.¹⁵ As a comparison, values of 11 and 8 nm for the gap of capacitors of SBR between carbon black aggregates were obtained

for low carbon black concentrations (30 phr) for a barrier potential of 0.1 eV and 0.2 eV, respectively.⁴³ In summary, we successfully estimated the gap spacing of the microcapacitors formed by the entrapped P α MSAN between adjacent MWNTs and its invariant behavior with the copolymer from both dielectric relaxation as well as the impedance formalism.

3.3. Amount of entrapped P α MSAN

As the gap spacing of the microcapacitors is unaffected by the copolymer, only the connectivity of the microcapacitors could tune the interfacial capacitance of the microcapacitor network. To gain further insight in the effect of various copolymers on the connectivity of the microcapacitors, the physical parameters characterizing the microcapacitor assembly will be estimated. Thereto, we employed the theoretical interlayer model developed by Steeman et al.⁴⁹ The model describes the complex permittivity of a three-phase blend (ϵ_b^*) comprising of filler, interlayer and matrix, in which filler particles enclosed with a layer of interfacial material are embedded in a matrix. The response of our blend system to the imposed electric field allows to allocate the various blend components to the relevant constituents of the model. The electric field response of entrapped P α MSAN chains between the MWNTs results in a substantial capacitance and thus, the former behaves as a material with high dielectric constant. This phenomenon is due to the partial screening of the entrapped P α MSAN (behaving as fillers) by the enveloped interlayer of conductive MWNTs embedded in the blend. A similar study has been performed by Steeman et al. for model composites of interfacially adsorbed water on spherical glass filler particles dispersed in a matrix of HDPE in order to estimate the amount of adsorbed water.^{50,51} The modelling of $\epsilon_b^*(\omega)$ is achieved by taking into account the respective complex permittivity and volume fractions of the filler ($\epsilon_f^*(\omega)$ and ϕ_f of P α MSAN), the interlayer ($\epsilon_l^*(\omega)$ and ϕ_l of MWNTs) and the matrix ($\epsilon_m^*(\omega)$ and ϕ_m of the blend with copolymer only). For the interlayer, ϕ_l was assumed to be constant (MWNT volume fraction in the blend) and the $\epsilon_l^*(\omega)$ was calculated using eq 9 in which the

capacitive contribution of the MWNTs was neglected ($\epsilon'_l(\omega) \approx 0$):

$$\epsilon_l^*(\omega) = i\epsilon_l''(\omega) = i\frac{\sigma'_{dc}\omega}{\epsilon_0} \quad (9)$$

The σ'_{dc} for MWNTs used in eq 9 is 10^4 S/cm.²⁷ Subsequently, ϵ_b^* can be estimated in the direction of any of the principal axes of the filler by incorporating the shape factor of the filler for that direction, and subsequently weighing the contributions with their relative occurrence. In this view, an experimental Debye-type dielectric interfacial peak observed in Figure 3b is a manifestation of a negligible distribution in filler dimensions and shape factors,⁴⁹ allowing to choose the appropriate form of the interlayer model:⁴⁹

$$\begin{aligned} \epsilon_b^*(\omega) &= \frac{\epsilon_f^*(\omega)\phi_f + \epsilon_l^*(\omega)\phi_l R + \epsilon_m^*(\omega)\phi_m S}{\phi_f + \phi_l R + \phi_m S} \\ R &= \frac{(1-n)\epsilon_l^*(\omega) + n\epsilon_f^*(\omega)}{\epsilon_l^*(\omega)} \\ S &= \frac{(n\epsilon_l^*(\omega) + (1-n)\epsilon_m^*(\omega))(n\epsilon_f^*(\omega) + (1-n)\epsilon_l^*(\omega)) + dn(1-n)(\epsilon_l^*(\omega) - \epsilon_m^*(\omega))(\epsilon_f^*(\omega) - \epsilon_l^*(\omega))}{\epsilon_l^*(\omega)\epsilon_m^*(\omega)} \\ d &= \frac{\phi_f}{\phi_f + \phi_l} \end{aligned} \quad (10)$$

During the estimation of ϵ_b^* , the first fitting parameter is n , which characterizes the shape of the polarized P α MSAN entrapped between the MWNTs, and is a measure of the interfacial polarization strength of a single microcapacitor. The other fitting parameter is the total volume fraction of the polarized P α MSAN (ϕ_f) enveloped by the MWNTs in the blend, which is correlated with the connectivity of the microcapacitors. In summary, from the interlayer model, the combined knowledge of the physical state and connectivity of the microcapacitors estimated respectively from the shape factor of P α MSAN in a single microcapacitor and the volume fraction of the entrapped P α MSAN in the blend determine the total dielectric interfacial polarization of the microcapacitors in the blends. In this regard, the various copolymers ability to generate and stabilize the biphasic morphology in order to pave a network of microcapacitors will be predicted by the combined knowledge of the

Figure 7. (a) Schematic of the proposed arrangement of the various components in the interlayer model used for modelling the complex permittivity spectra for blends with MWNTs and copolymer. (b) Complex permittivity spectra of biphasic 40/60 P α MSAN/PMMA blend with 0.5 wt% MWNTs and 0.25 wt% short rcp (34 kg/mol), long rcp (270 kg/mol) and short bcp (37 kg/mol) at 220 °C. The fitted spectra obtained using the interlayer model (eq 10) are shown as lines and the values of the fitting parameters are indicated.

microcapacitor behavior and the interlayer model.

We analyze the interfacial dielectric response of entrapped P α MSAN filler sandwiched between two neighboring MWNTs mimicking an interlayer, whose possible arrangements are

depicted in the schematic presented in Figure 7a. As a proof of concept, Figure 7b shows the
 complex dielectric permittivity spectrum of a biphasic blend with 0.25 wt% long rcp (270
 kg/mol) and 0.5 wt% MWNTs at 220 °C, whose permittivity and impedance response are
 presented in Figure 3b and Figure 4a. For comparison, the spectra of blends with short rcp
 and short bcp are also shown. An accurate prediction of the contribution from interfacial
 polarization is obtained for the various blends, as shown in Figure 7b (lines). The fit at
 low frequencies is not accurate due to contributions of electrode polarization, which are not
 taken into account in the model. The fitting parameter ' n ' is estimated to be $\approx 10^{-5}$ and is
 unaffected by the copolymer type and concentration. This further warrants that the copoly-
 mer does not affect the state of dispersion of the MWNTs. A comment on the physical
 state and the plausible network formed by the entrapped P α MSAN between neighboring
 MWNTs is done. With respect to the former, fillers with ' n ' $\rightarrow 0$ are predicted to behave
 rod-like along the direction of the electric field.⁴⁹ This is in agreement with the fact that
 the gap spacing of the P α MSAN microcapacitor is larger than the thickness of the polarized
 P α MSAN region forming the microcapacitor. The latter can be understood by the fact that
 the microcapacitor is characterized by a very localized polarization zone on the MWNTs.
 We believe the rod-like P α MSAN regions between adjacent MWNTs are bridging the neigh-
 boring MWNTs (Figure 7a). It should be noted that ' n ' $\rightarrow 0$ does not imply an anisotropy
 in the MWNT network but rather that the dominant contributions originate from the po-
 larized P α MSAN microcapacitors oriented along the electric field. This was confirmed by
 verifying that any contributions with larger ' n ' values in eq 10 resulted in significantly lower
 dielectric strengths. The polymer bridges between neighboring MWNT particles determine
 the properties of the MWNT network. Similar formation of glassy-like polymer bridges of
 styrene butadiene rubber between two carbon black aggregates were found on the basis of
 the microcapacitor model.^{43,52} Mainly systems with strong polymer-filler interactions exhib-
 ited formation of polymer bridges between neighboring filler particles, which resulted in a
 reduced chain mobility close to the filler surface and governed the viscoelastic response of

the filler network.⁴³

To gain further insight in the effect of various copolymers on the connectivity of the microcapacitors, another physical parameter linked with the connectivity, namely the volume fraction of entrapped P α MSAN (ϕ_f) between the surfaces of MWNTs is estimated. Figure 7b shows that blends with short bcp exhibit an increase in the fitting parameter ϕ_f by a decade as compared to blends with short rcp, and blends with long rcp show a further increase in ϕ_f by more than a decade. To gain further insight in the effect of various rcp and bcp on the filler connectivity, the dependence of the volume fraction of the entrapped P α MSAN between neighboring MWNTs on the concentrations of various rcp and bcp is plotted in Figure 8. The dependence of ϕ_f on the copolymer concentration exhibits a similar behavior as the interfacial capacitance in the presence of various rcp and bcp (Figure 5). Eq 5 shows that the total capacitance area of polarized P α MSAN between MWNTs is proportional to the interfacial capacitance. Therefore, the total capacitance area is expected to exhibit a similar behavior as the estimated ϕ_f , as both physical parameters account for the connectivity of the microcapacitors. A pronounced increase by 4 orders of magnitude in the volume fraction of the P α MSAN microcapacitors is in conjunction with the increasing interfacial capacitance with various copolymers. The increase in the connectivity of the microcapacitors and the interfacial capacitance of the entrapped P α MSAN network between neighboring MWNTs results from the ability of the copolymer to increase the refinement and to improve the connectivity of the P α MSAN phase containing the MWNTs. This refinement and improved connectivity in the presence of long rcp and bcp irrespective of its M_w was reported in our recent work.⁷ In summary, the interlayer model predicts an increase in the volume fraction of entrapped rod-like P α MSAN regions by 4 decades with an increase in the interfacial capacitance of the MWNT-P α MSAN microcapacitor network.

Figure 8. Volume fraction of entrapped P α MSAN obtained as a fitting parameter using eq 10 versus rcp and bcp concentration for biphasic 40/60 P α MSAN/PMMA blends with 0.5 wt% MWNTs at 220 °C.

3.4. Modeling the MWNT-P α MSAN interfacial capacitance

The parameters characterizing the physical state (gap spacing) and connectivity of the entrapped P α MSAN-MWNTs (volume fraction of P α MSAN) will be used to predict the interfacial capacitance. We envisage that an estimation of the volume fraction of the entrapped polymer would incorporate the effect of the copolymer on the connectivity of the MWNTs-entrapped P α MSAN assembly. This in turn would allow to estimate the total number of capacitors contributing to the estimated interfacial capacitance in our blend system. As the charge transfer path is contingent upon the connectivity of the MWNTs-entrapped P α MSAN assembly and the gap spacing is invariant with copolymer, only an increase in the connectivity of the microcapacitors would affect the interfacial capacitance of the microcapacitor assembly. The underlying motivation for the ensuing discussions is the fact that a combined estimation of the total number of capacitors and the individual capacitance (from the gap

spacing) would allow us to predict the total interfacial capacitance of the microcapacitor assembly in the blend system. In conclusion, the estimated total interfacial capacitance is a fingerprint of the connectivity of the microcapacitor assembly or the biphasic morphology, whose estimated values are contingent on the copolymers architecture and concentration. As a first approximation, the product of the calculated individual capacitance (C_i) and the number of capacitors (N) yields the total interfacial capacitance (C_{int}):

$$C_{int} = C_i N \quad (11)$$

The shape of each individual capacitor irrespective of the MWNTs arrangement can be approximated by a cylinder, leading to:

$$C_i = \epsilon_0 \epsilon \frac{A}{\delta} \quad (12)$$

with A the capacitor area and δ its thickness. The ratio of the total volume of capacitors (V_t) to the individual capacitor volume (V_i) is used to calculate the number of capacitors (N):

$$N = \frac{V_t}{V_i} \quad (13)$$

The product of the estimated volume fraction of P α MSAN contributing to the microcapacitors (ϕ_f) using the interlayer model (Figure 8b) and the blend volume is used to calculate the total volume of capacitors (V_t):

$$V_t = \phi_f V_b \quad (14)$$

whereas V_i is the volume of a cylinder:

$$V_i = \delta A \quad (15)$$

Upon substitution of C_i and N from eq 12 - 13 in eq 11 using eq 14 - 15, the C_{int} is found to be independent of the polarization area and proportional to ϕ_f :

$$C_{int} = \frac{\epsilon_0 \epsilon \phi_f V_b}{\delta^2} \quad (16)$$

Other parameters in eq 16 are unaffected by the connectivity of the MWNT-P α MSAN microcapacitor network. It is imperative to emphasize that the total interfacial capacitance of the microcapacitor assembly in eq 16 is contingent on the gap spacing estimated using the FIT model and the experimental interfacial relaxation time (eq 8), and the volume fraction of the microcapacitors obtained from the interlayer model and the experimental interfacial relaxation strength (eq 10). The thus obtained total interfacial capacitances for blends with various copolymers and with increasing copolymer concentration are presented in Figure 9. The interfacial capacitance obtained from the fitting of the impedance response of the blends (Figure 4a and b) presented in Figure 5 is also shown for comparison in Figure 9. Upon comparison of the magnitude of the interfacial capacitance determined from the circuit fitting of the impedance response of the blends with that estimated from the response of the microcapacitor assembly in the blends using the FIT and interlayer models, a remarkable agreement is obtained in Figure 9. It is imperative to emphasize that the underlying rationale in the estimation of the total capacitance has emanated from the unified formalism of experimentally determined relaxation times analyzed with the FIT model in combination with experimentally determined relaxation strengths analyzed with the interlayer model. Thus, the adopted approach allows to separately obtain the contributions from each capacitor as well their connectivity and the fact that recombining the information leads to a good description proves the validity of the approach.

A remarkable agreement of the magnitude of the interfacial capacitance determined from the circuit fitting of the impedance response of the blends with that estimated from the microcapacitor assembly in the blends using various models in Figure 9 entails some discussion. Upon

increase of the connectivity of P α MSAN laden with MWNTs, there are more connections of
 the individual microcapacitors entrapped between the surface of MWNTs, whereas the gap
 of each microcapacitor is not affected. Even though the charges take the least resistive path,
 the unaltered gap of the microcapacitors in the presence of various copolymers ensures that
 we do not affect the local charge transfer path or resistance between the microcapacitors.
 Hence, upon increasing the refinement and continuity of the P α MSAN phase with copoly-
 mers, only the effect of the connectivity of the microcapacitors orchestrates the estimated
 interfacial capacitance. In this regard, a proportional decrease in the interfacial resistance
 and an increase in the interfacial capacitance with increased number of capacitors is expected
 for a parallel combination of microcapacitors ($C_{tot} = \sum C_i = n C_i$ and $R_{tot} = \frac{1}{\sum 1/R_i} = \frac{R_i}{n}$)
 and a reverse trend is expected for a series combination ($C_{tot} = \frac{1}{\sum 1/C_i} = \frac{C_i}{n}$ and $R_{tot} =$
 $\sum R_i = n R_i$). However, the interfacial relaxation time of the microcapacitors ($\tau_{interface} =$
 $\frac{1}{RC} = \frac{1}{R_i C_i}$) is unaffected by the choice of the charge transfer path (series or parallel). The
 latter clarifies why one single relaxation time is obtained for all systems, irrespective of the
 complex connections of the different (but identical) micro-capacitors. Furthermore, we ob-
 serve an increase in the interfacial capacitance and a proportional decrease in the interfacial
 resistance with increasing amount of the copolymer (Figure 3). This suggests that the length
 of each path for charge transfer is unaffected with refinement, but an increase in the number
 of connections is achieved. Thus, we are measuring the increased amount of parallel RC
 circuits upon copolymer addition. With regard to the biphasic morphology, for disconnected
 P α MSAN domains with MWNTs, the parallel contribution of the charge transfer through
 an RC network of P α MSAN and MWNTs to the interfacial capacitance is restricted. By
 changing the copolymer type, M_w or concentration, morphology refinement and increased
 continuity of the P α MSAN phase resulted in an increase in the parallel networks of the en-
 trapped P α MSAN microcapacitors between the surfaces of adjacent MWNTs. This leads to
 an increase in the interfacial capacitance by around 5 decades in magnitude for percolated
 blends as compared to blends lacking interconnectivity of the capacitors. The interlayer

model also comments on the correlation of the physical state of the microcapacitors with 1
their connectivity depending upon the state of polarization of the microcapacitors. In this 2
regard, an assembly of conducting-dielectric elements with rod-like fillers tends to exhibit 3
parallel connections.⁴⁹ Hence, the formation of parallel elements in the limit of rod-like filler 4
particles of entrapped P α MSAN between the MWNTs renders strong support to our finding 5
of an augmented parallel network formation of microcapacitors upon compatibilization. 6
In summary, the dielectric response of the biphasic system and its constituents in combina- 7
tion with knowledge of the interfacial dynamics is sufficient to predict the interfacial capac- 8
itance and the network formation of the microcapacitors. Interestingly, the phenomenon is 9
a signature of the connectivity of the biphasic morphology, even though it is fundamentally 10
dissimilar to increasing conductivity. In summary, the results presented in Figure 9 establish 11
a novel methodology for predicting the interfacial capacitance and probing the connectivity 12
of microcapacitors in complex systems. 13

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Figure 9. Interfacial capacitance of the MWNTs-entrapped P α MSAN network obtained from Figure 5 (designated as RQ circuit), and from eq 16 versus rcp/bcp concentration for bi-phasic 40/60 P α MSAN/PMMA blends with 0.5 wt% MWNTs at 220 °C. The interlayer model was used to determine ϕ_f and the fluctuation induced tunneling model was used to determine δ in eq 16. Inset: Schematic of the biphasic morphology with increasing MWNT interfacial capacitance.

4. Conclusions

We report for the first time an effect of copolymers architecture, molecular weight and concentration on the dielectric MWNT-P α MSAN interfacial capacitance in phase separated 40/60 (wt%/ wt%) P α MSAN/PMMA blends with 0.5 wt% MWNTs. Compatibilization was achieved upon interfacial segregation of a block (bcp) or random copolymer (rcp) of PS-PMMA, while the MWNTs selectively localized in the P α MSAN phase. The AC conductivity and dielectric properties reflect local motions of charge carriers governed by the mesoscopic length scales of the materials. At high frequencies (above 1 MHz) the electrons hop between the adjacent MWNTs, whereas at intermediate frequencies, the electrons of the MWNTs tunnel through the barriers imposed by the entrapped P α MSAN.

The latter phenomenon results in an interfacial dielectric relaxation peak, similar to that
 in MWNTs-P α MSAN composites. To further quantify the MWNT-P α MSAN interfacial
 dielectric properties in the blends, an equivalent electrical circuit was developed and its
 parameters were determined from the Nyquist plots. Adjacent MWNTs entrapping a thin
 dielectric layer of P α MSAN form a microcapacitor, represented by an RC element. The total
 interfacial capacitance increases with addition of copolymer, whereas the total interfacial
 resistance decreases. The effect of various copolymers on the physical characteristics
 of the microcapacitor network, i.e. the gap spacing of the capacitors and the volume
 fraction of the entrapped P α MSAN chains between the MWNTs was elucidated. Using
 the fluctuation induced tunneling (FIT) model, the gap spacing was calculated from the
 interfacial relaxation time, obtained from either the product of the interfacial resistance
 and capacitance or from HN fitting of the “conduction free” dielectric spectra, giving
 similar results. The volume fraction of entrapped P α MSAN chains was estimated using the
 dielectric interlayer model. The effect of the copolymer on the gap spacing was negligible,
 whereas the volume fraction of entrapped P α MSAN chains increased by 4 decades upon
 effective compatibilization. This was attributed to an increase in the connectivity of the
 dispersed microcapacitors of entrapped P α MSAN between MWNTs without changing the
 characteristics of each capacitor. Combining the thickness of each microcapacitor and
 the volume fraction of entrapped P α MSAN contributing to the microcapacitor network
 allowed to estimate the total interfacial capacitance. A remarkable agreement between
 the total interfacial capacitance obtained using aforementioned method and the interfacial
 capacitance measured as a fitting parameter in the Nyquist fitting of the impedance
 response was obtained. In conclusion, effective compatibilization led to an increase in
 the interfacial capacitance originating from the microcapacitor network of MWNTs in
 the P α MSAN phase. It is known that the state of percolation and the local organization
 of the MWNTs governs the performance of a material, like its resistance against crack
 initiation and crack propagation.⁵³ Our findings can be used to independently tune the

MWNT network percolation (via the copolymers) as well as the inter-MWNT distance 1
(via the MWNT concentration) allowing to tailor physical properties governed by various 2
length scales of the material. In addition, the developed characterization approach allows 3
to separately analyze the local microcapacitor properties as well as their connectivity. 4

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Table of Contents

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