PP/ABS Blends with Carbon Black: Morphology and Electrical Properties

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ABSTRACT: Phase morphology of melt-mixed polypropylene (PP)/acrylonitrile-butadiene-styrene (ABS) blends was found to be blend ratio dependent, viz., matrix-particle dispersed type of morphology which was observed up to 30 wt % of ABS level beyond which the morphology showed co-continuous type. The domain size of 80/20 PP/ABS blends was found to decrease significantly at 10 wt % carbon black (CB) level, and in case of 70/30 blends morphology was transformed into co-continuous type in the presence of CB, which was retained up to 60 wt % ABS. The finer morphological features were associated with the compatibilizing action of CB particles. Continuous network was achieved through aggregated CB particles predominantly in the PP phase wherein one could find CB-rich PP phase and CB-less PP phase. Solution experiments further supported the existence of CB particles preferentially in the PP phase. AC electrical conductivity measurements indicated a 3D network-like structure of CB aggregates in the co-continuous compositions which showed enhanced electrical conductivity as compared to the matrix-dispersed type of morphology in 80/20 PP/ABS blends which exhibited insulating behavior. On increasing ABS content in the blends the electrical conductivity decreased progressively due to a difficulty in retaining 3D continuous network of CB aggregates especially at 40/60 composition. Increased processing temperature led to a higher electrical conductivity in the respective blends. Dielectric measurements revealed the existence of metallic type of conduction in the co-continuous compositions. However, 80/20 blends showed low ε' value. Overall, structure property relationship studies were conducted in PP/ABS blends with CB. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 998–1004, 2009

Key words: blends; conducting filler; morphology; dispersion; electrical conductivity

INTRODUCTION

Polymer blends are a well recognized class of materials which can be tailored according to application requirements and have received immense interest in both industrial and academic fields due to the possibility to exploit the unique morphology associated with blend compositions. In this context the strategy toward "double percolation" phenomenon using co-continuous morphology generates a great deal of technological interest due to the possibility to achieve electrically conducting composites by restricting conducting fillers in one of the phases or at the interface of a co-continuous blends.[1–5] However, fillers have a tendency to migrate to the other phase during melt-mixing even if thermodynamic factors viz. surface energy difference between the polymer matrix and the filler is not favorable.[6] In addition, kinetic factors are also found to take a lead role in pushing the filler from one phase to the other which sometimes dominate over the melt viscosity ratio factor and influences the state of dispersion of filler in a given phase.[7] Moreover, aggregated nature of the filler poses a difficulty in obtaining continuous pathway at low filler concentrations.

Numerous studies have been conducted in conducting filler-based polymer composites.[8] In this context, polymer blends with carbon black (CB) as conducting filler have been studied in various systems. Polypropylene (PP)/high-density polyethylene (HDPE) blends with addition of CB was studied to understand the influence of HDPE content, CB structure, and PP melt viscosity on morphology and electrical conductivity of the injection-molded specimens.[9] CB was found to be preferentially located in HDPE phase and the effect of "double percolation" was observed in achieving lower electrical percolation threshold in 70/30 co-continuous blends. A
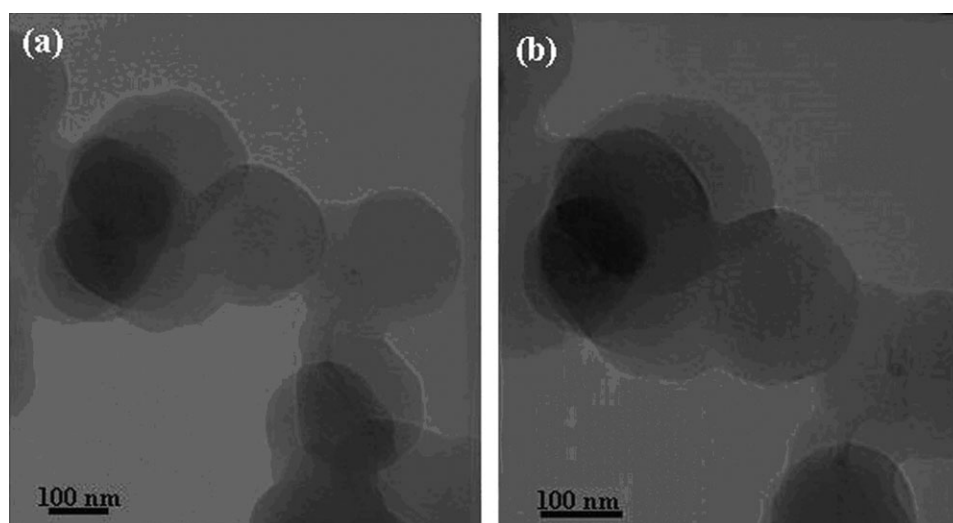
Figure 1 Transmission electron micrograph of carbon black (Vulcan XC72). (a) Lower magnification; (b) higher magnification.

similar strategy was followed in obtaining sensor materials based on PP/nylon6 (PA6) blends in which conducting CB particles were preferentially attracted to the polar PA6, which has a surface tension value close to the CB.[10] Enhancement of electrical conductivity in these blends was found to be due to the formation of honeycomb-like structures with selective localization of CB particles at the interface giving rise to segregated conductive networks. This typical morphological feature led to the percolation threshold at a lower level of CB. One of the very earlier works on dispersion of CB in different polymer blends was reported by Sumita et al. in which three different polymer blend systems viz., HDPE/PP, PP/PMMA, and HDPE/PMMA were used.[11] Based on the morphological observation in HDPE/PP blends they concluded that the majority of CB particles were distributed in the HDPE phase, and within this phase CB particles were relatively homogeneously dispersed. However, in PMMA/PP blends, the majority of CB particles were distributed in the PMMA phase and especially at the interface of the two polymers. Further, an envelope formation of CB particles was seen around each PMMA domain. Similar dispersion of CB was observed in the HDPE/PMMA blend matrix. In this case, CB filler was located in the HDPE phase and was typically concentrated at the interface of the two polymers via an envelope formation. In this connection, wetting coefficients for the various blend systems were calculated and the dispersion of CB was predicted and experimentally verified.

PP is a versatile commodity plastic; however, it has a shortcoming of poor impact resistance. Blending PP with rubbery polymers like acrylonitrile-butadiene-styrene (ABS)[12] is an industrial practice to improve the impact resistance with suitable modification of the interface.[13] However, conducting filler-based PP/ABS blends have not been explored much which can find application in antistatic materials, EMI shielding materials, capacitors, and so on.

The motivation of this work is to study the effect of CB on the morphology, electrical conductivity, and dielectric properties of PP/ABS blends. It is also aimed to understand the role of specific morphology of these blends in influencing the electrical conductivity of the PP/ABS+CB composites. Dielectric properties have been studied in this connection as well.

EXPERIMENTAL

Materials and specimen preparation

PP was obtained from Reliance Industries Ltd. (Mumbai, India) (H200MA) with melt flow index of 23 (here after assigned as 23P). ABS copolymer (Absolac-120, with composition as: acrylonitrile 24 wt %, styrene 59.5 wt %, and rubber content 16.5 wt %) was obtained from Bayer India Ltd. (Mumbai, India). Carbon black (CB, grade Vulcan XC72) was obtained from Cabot India Ltd. Transmission electron micrograph shows (Fig. 1) the particle size of CB used is in between 100 and 200 nm.

PP/ABS blends compounded with and without CB were prepared by melt-mixing in a conical twin-screw extruder (Micro 5, DSM Research, Netherlands) at 260°C with a rotational speed of 150 rpm for 15 min. All blend components were predried in vacuum oven at 80°C for 24 h. During melt mixing a mixing protocol was followed wherein PP and CB was melt mixed for 10 min followed by ABS for 5 min.

Injection-molded samples (according to ASTM D 638, Type V) were prepared using mini-injection

molding machine from DSM Research Netherlands. The injection-molding parameters maintained for all the compositions were injection pressure 3 bar, melt temperature 260°C, mold temperature 60°C, holding time 60 s, and cooling time 2–3 min.

Characterization

AC conductivity

The AC conductivity measurements were performed on the injection-molded samples (across the thickness) in the frequency range between 10^{-1} and 10^6 Hz using Alpha high resolution analyzer coupled to a Novocontrol interface (broad band dielectric converter). The DC conductivity of the samples was determined from the AC conductivity plots in the region of low-frequency plateau by fitting power law equation ($\sigma_{AC} = \sigma_{DC} + A\omega^n$, $0 < n < 1$).[14]

Scanning electron microscopy

Morphological features and state of dispersion or preferential localization of CB in blends were studied by SEM. Extrudate samples were cryofractured in liquid nitrogen and selectively etched in the THF to remove ABS. The etched surface was gold sputtered to avoid the charging of the sample. These samples were then observed under SEM using Hitachi S3400N.

Solution experiment

The composites were dissolved in the respective solvents so as to completely remove selectively one of the phases. Fifty milligrams of samples were cut into small pieces and then kept in the respective solvents for 4 days. The composites were dissolved in THF to remove the ABS phase and were also dissolved in hot xylene to remove the PP phase. The color of the resulting solution provides an idea about the location of the CB particles in the blends.

RESULTS AND DISCUSSION

Morphology of PP/ABS+CB composites

Figure 2 shows the scanning electron micrographs of cryofractured and etched surfaces of PP/ABS blends and PP/ABS+CB composites where ABS phase has been removed preferentially to observe the morphological features corresponding to varied blend compositions. It is observed that neat PP/ABS blends up to 30 wt % ABS content exhibit matrix-dispersed droplet kind of morphology. Interestingly, the droplet size of ABS is found to decrease drastically in the presence of 10 wt % CB content in 80/20 PP/ABS blends, however, the morphology of the 70/30
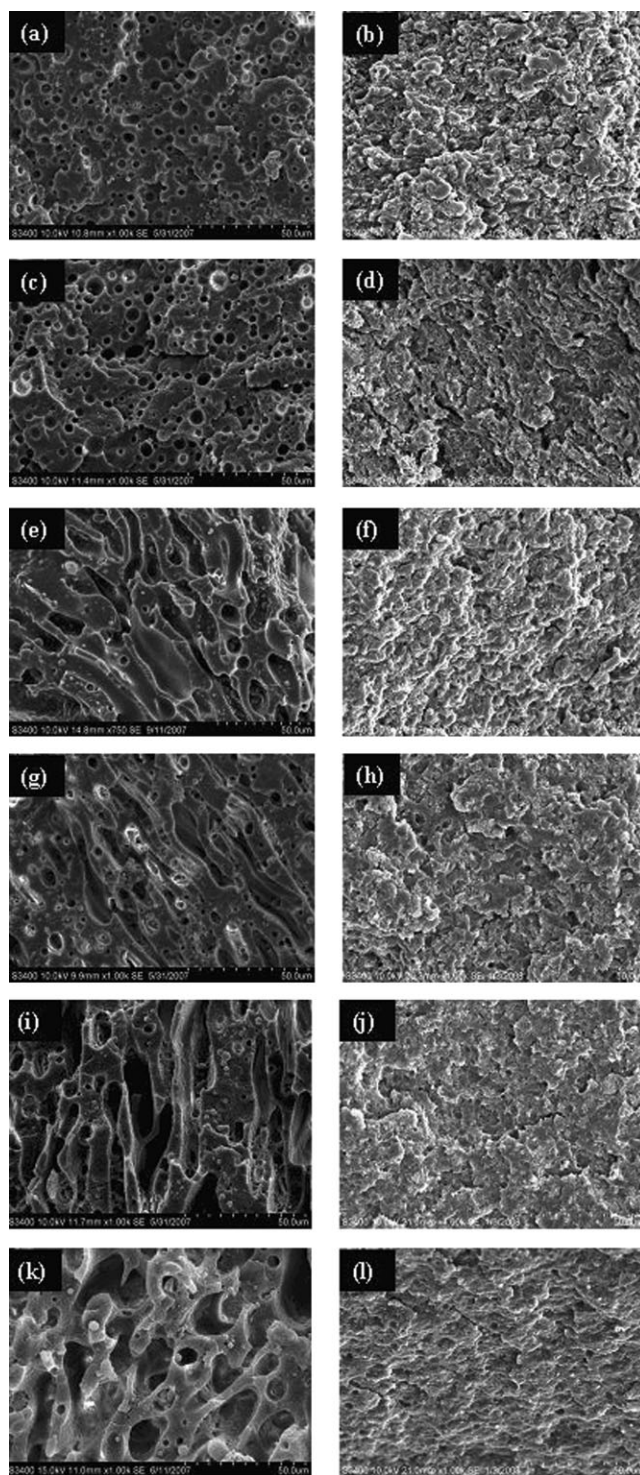

Figure 2 SEM micrographs of PP/ABS blends and PP/ABS blends with CB (a) 80/20 PP/ABS, (b) 80/20 PP/ABS+CB (10 wt %), (c) 70/30 PP/ABS, (d) 70/30 PP/ABS+CB (10 wt %), (e) 60/40 PP/ABS, (f) 60/40 PP/ABS+CB (10 wt %), (g) 50/50 PP/ABS, (h) 50/50 PP/ABS+CB (10 wt %), (i) 45/55 PP/ABS, (j) 45/55 PP/ABS+CB (10 wt %), (k) 40/60 PP/ABS, (l) 40/40 PP/ABS+CB (10 wt %).

PP/ABS blends at 10 wt % CB level manifest co-continuous type. The co-continuous type of morphology is found to persist up to 60 wt % ABS content, however, at 40/60 PP/ABS composition along with co-continuous feature subinclusions of ABS are also found to be dominant. PP/ABS blends containing 40–60 wt % ABS level exhibit coarse co-continuous features whereas these blends with 10 wt % CB exhibit a finer morphological feature. In general, the observation of finer morphological structure in these compositions indicates the influence of CB in stabilizing the morphology, which is also reported for several other filled systems. The fine morphological features are probably associated with the compatibilizing action of CB suppressing the coalescence phenomena between the droplets; however, the compatibilizing action of CB is probably related to the kinetic barrier imposed by CB particles which are otherwise not allowing the two adjacent droplets to coalesce together. The localization of filler in one of the phases in blends leads to an increase in the melt viscosity of the specific phase resulting in the suppression of coalescence.[15] Such phenomenon has earlier been reported in case of PA6/PVDF blends in presence of nanoclay.[16] The presence of clay at the interphase as well as in the bulk has been believed to be the reason behind such compatibilizing action of nanoclay. This phenomenon of compatibilization by solid fillers have also been reported for different blends systems with fillers of different geometrical shapes and sizes such as PA6/poly(ethylene-ran-propylene) rubber blends with organoclay,[17] PP/PS blends with layered silicates,[18] PE/PS blends with CB,[15] and PP/ABS blends with MWNT.[19]

It is also observed from Figures 2 and 3 that CB particles essentially form aggregated structure wherein they are predominantly dispersed in the PP phase because of its lower melt viscosity than ABS. Thermodynamic considerations involving the calculations of interfacial energy differences reveal the affinity of CB particles toward the ABS phase in PP/ABS blends. It is worthy to mention that within the PP phase one can observe CB-rich PP phase consisting of continuous network of aggregated CB particles along with CB-less PP phase, where aggregated CB particles are not observed. This observation is found to be consistent when ABS content is varied from 30 to 55 wt % in which a 3D network like structure is formed by CB-rich PP phase which possibly forms an interface with ABS in co-continuous type of morphology. At 20 wt % ABS level even if the aggregated feature of CB exists but a three-dimensional network is not formed due to the matrix-dispersed type of morphology. At 45/55 PP/ABS composition there seems to be an onset of breakdown of aggregates of CB particles in the bulk of the PP phase. At 60 wt % ABS level, instead
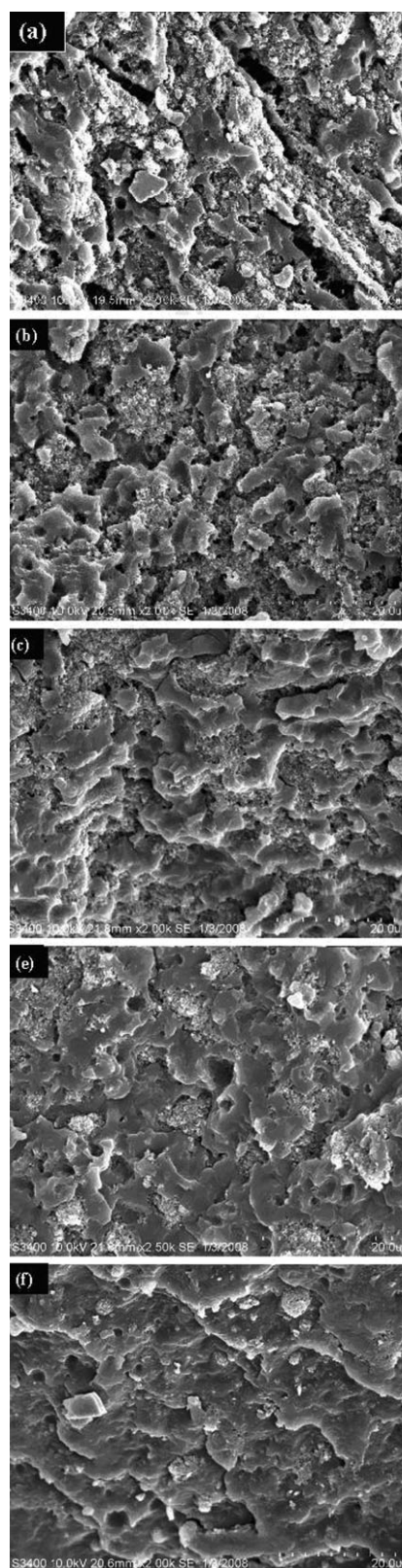

Figure 3 Dispersion of CB particles in PP/ABS blends (a) 80/20 PP/ABS+CB (10 wt %), (b) 70/30 PP/ABS+CB (10 wt %), (c) 60/40 PP/ABS+CB (10 wt %), (d) 50/50 PP/ABS+CB (10 wt %), (e) 45/55 PP/ABS+CB (10 wt %), (f) 40/60 PP/ABS+CB (10 wt %).
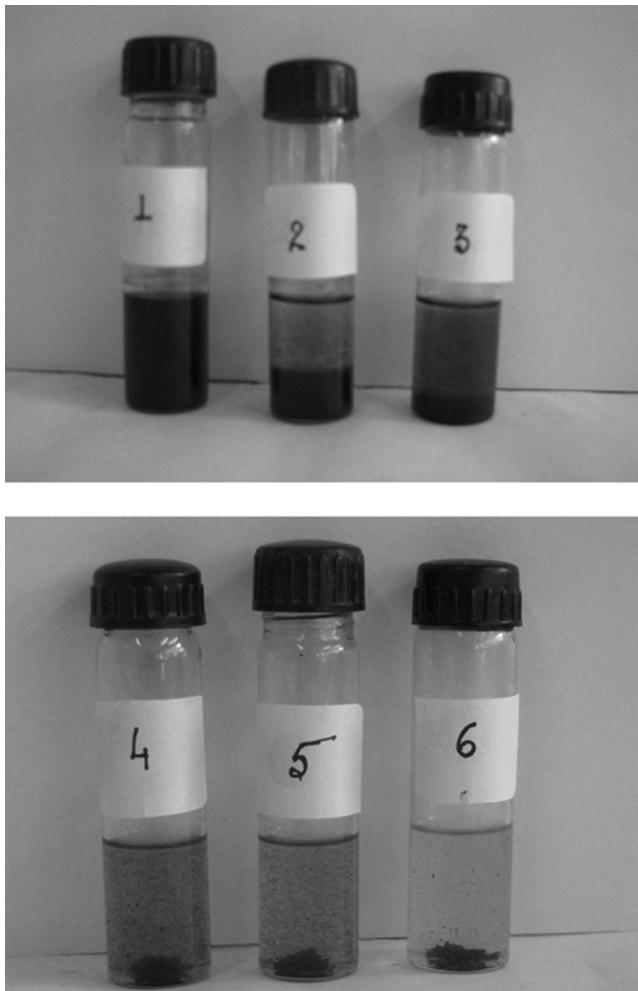
Figure 4 Solution experiment to investigate any preferential localization of CB in one of the phases: (1) 80/20, (2) 70/30, (3) 40/60 in hot xylene, (4) 80/20, (5) 70/30, (6) 40/60 PP/ABS blends in THF.

of aggregated feature one can observe finely distributed CB particles throughout the PP phase since increasing amount of ABS enhances overall melt viscosity of the system thereby increasing shear stress which may be responsible for breakdown of the aggregates. In general, during melt mixing part of the CB particles are found to migrate toward the ABS phase depending on the blend compositions which is controlled by melt viscosity ratio of the two phases wherein the extent of migration/redistribution of CB particles is reduced with increase in ABS content because of the difficulty to diffuse through the more viscous ABS phase.

Solution experiment

Solution experiments were carried out with PP/ABS blends of three compositions viz., 80/20, 70/30, and 40/60 to investigate any preferential localization of CB particles in one of the phases. It is observed (Fig. 4)

that CB particles are essentially located in PP phase as the solution turned strong black in color irrespective of blends composition once the specimens are boiled with xylene. However, on removing ABS phase selectively using boiling THF, the 80/20 composition showed strong black color of the solution whereas 70/30 and 40/60 shows less black color progressively as the ABS content increases in the composition. The results further indicate that the migration of the filler becomes more difficult to the ABS phase as the ABS content is increased in the blend compositions.

AC electrical conductivity and dielectric properties

Figure 5 shows the variation of AC conductivity with frequency in PP/ABS blends with 10 wt % CB where ABS content is varied from 20 to 60 wt %. In case of 80/20 blends with CB, AC electrical conductivity increases with increase in frequency without showing a DC plateau in our measured range of frequency and is found to be in the insulating range. However, on increasing the ABS content, the nature of the plot changes where one can observe a DC plateau for a range of frequency followed by an increase in conductivity beyond a critical frequency (ω_c) following the Jonscher's universal power law.[12] It is evident that 80/20 blends with 10 wt % CB exhibit insulating behavior presumably due to the matrix-dispersed type of morphology wherein CB-rich PP phase could not form continuous path as evident from SEM micrographs. However, blends with 30–40 wt % ABS content show a significant increase in DC conductivity for a wide range of frequency with increase in critical frequency (indicated from the values of ω_c). This result together with the morphological observation suggests that the significant increase in conductivity is related to the change in type of morphology wherein CB-rich PP phase could form a continuous pathway which is three dimensionally connected. This observation is explained by the "double percolation" phenomenon where conducting CB particles are found to restrict in one of the phases (PP phase) of co-continuous PP/ABS blends. One can even observe from the SEM micrographs the existence of geometrical networks of aggregated CB particles at the interface. Further, increase in ABS level beyond a critical concentration, however, led to a decrease in conductivity in which 40/60 blends showed the lowest value of electrical conductivity presumably due to change in co-continuous structure and the morphological features associated with CB aggregates induced geometrical network which is absent in 40/60 PP/ABS blends.

Dependence of AC electrical conductivity with mixing temperature is found to be significant in achieving lower electrical percolation threshold and
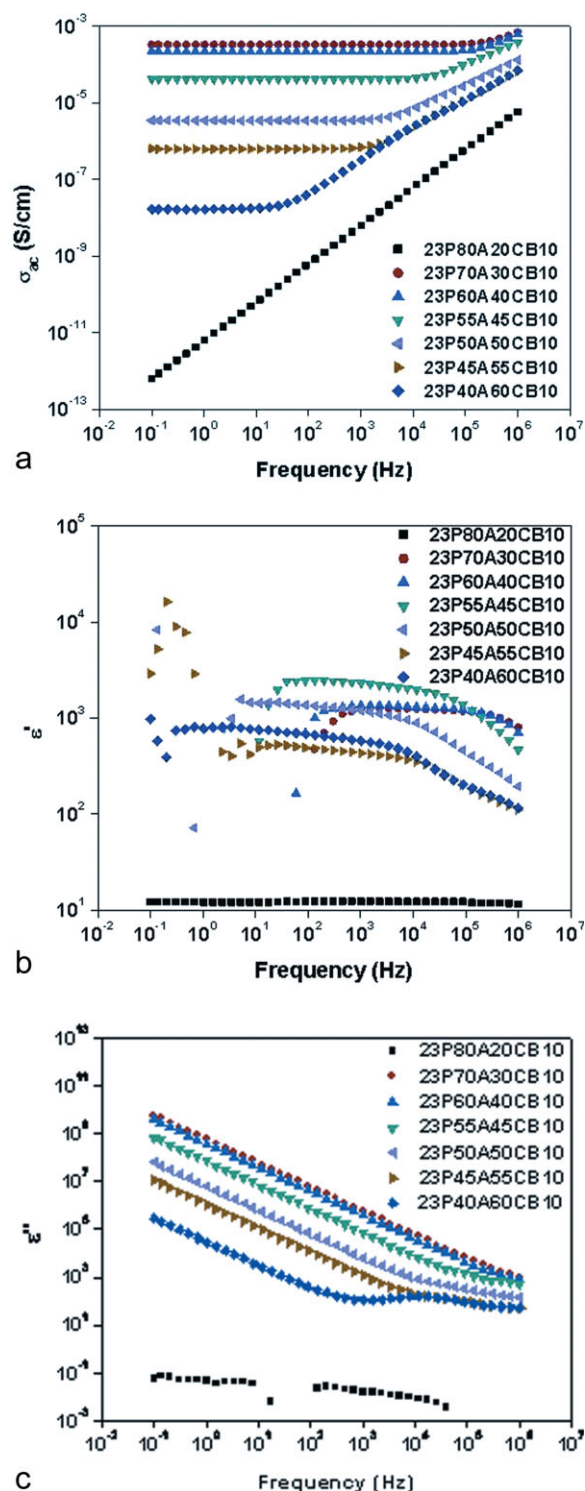
temperature. It is observed that higher mixing temperature of 260°C leads to a well-defined percolated network by aggregated CB particles, which is otherwise lower in conductivity when processed at 240°C. It seems that higher mixing temperature of processing helps in restricting the filler in one of the phases to achieve a continuous pathway.

In case of 80/20 PP/ABS blend with 10 wt % CB, permittivity (ε') values are found to be independent of frequency [Fig. 5(b)]. However, blends with 30–40 wt % ABS showed higher values of ε' at higher frequency and subsequently ε' could not be measured at lower frequencies indicating the formation of conducting percolating network provided by the CB particles. This observation is consistent with other blend compositions, however, for intermediate values of conductivity, ε' could be measured for a wider range of frequencies. Overall, the dielectric values are almost of the same order of magnitude once three-dimensional network-like structures has been achieved and are found to be much higher than 80/20 composition.

Typically two types of dielectric losses have been identified in polymers either due to the dipole-segmental loss or dipole group loss.[20] The appearance of loss is associated with the mobility of the polymer chains in the amorphous parts. It is reported that polar substituent in the side chains gives rise to dipole group loss which may also occur below the glass transition temperature of the polymer since the relaxation time for such groups is smaller than the main chain segments and hence they retain their mobility even at lower temperature where the segments in the main chain are practically immobile. This manifests a peak in the ε'' plots which can be clearly seen for 40/60 PP/ABS blends with 10 wt % CB associated with ABS chains [Fig. 5(c)]. It is also evident that below percolation threshold (in case of 80/20 PP/ABS) the ε' values are nearly constant and there are small changes in ε'' values but show significantly different behavior above percolation (70/30 blend composition onwards). Once percolation has been achieved at 10 wt % CB, the restriction in the mobility of the chains is believed to be a dominant factor governing the ε'' values.

Figure 5 (a) AC electrical conductivity of PP/ABS+CB composites with varying blend compositions. (b) Permittivity versus frequency in PP/ABS+CB composites with change in blends compositions. (c) Dielectric loss versus frequency in PP/ABS+CB composites with change in blends compositions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

higher electrical conductivity at the same CB loading of 10 wt %. Table I shows the comparison of DC conductivity of PP/ABS blends at different mixing

TABLE I
Comparison of DC Electrical Conductivity of PP/ABS+CB Composites at Two Different Mixing Temperatures

Samples	DC conductivity at 240°C (S/cm)	DC conductivity at 260°C (S/cm)
23P80A20CB10	3.18×10^{-9}	1.083×10^{-10}
23P60A40CB10	2.17×10^{-5}	2.184×10^{-4}
23P45A55CB10	1.41×10^{-12}	6.337×10^{-7}

SUMMARY AND CONCLUSIONS

PP/ABS blends have been melt mixed in a conical twin screw extruder and the morphology is found to be compositional dependent, matrix-particle dispersed type of morphology is observed up to 30 wt % of ABS level beyond which the morphology shows co-continuous type. On addition of 10 wt % CB in the respective PP/ABS blends the particle-dispersed type of morphology at 30 wt % ABS level is transformed to co-continuous structure which persists up to 60 wt % of ABS level. It is found that both the types of morphology become finer in the presence of CB indicating the compatibilizing action of CB. It is observed that co-continuous network is achieved through aggregated CB particles predominantly in the PP phase in which one can also find CB-rich PP phase and CB-less PP phase. Solution experiments further support the existence of CB particles preferentially in the PP phase. AC electrical conductivity measurements reveal a 3D network-like structure of CB aggregates in the co-continuous compositions, which show enhanced electrical conductivity as compared to the matrix-dispersed type of morphology in 80/20 PP/ABS blends which remains insulating. The enhanced electrical conductivity of 70/30 PP/ABS blends in the presence of CB is presumably due to the "double percolation" phenomenon achieved through co-continuous morphology. However, on increasing ABS content in the blends the electrical conductivity decreases progressively due to a difficulty in retaining 3D continuous network of CB aggregates especially at 40/60 composition where melt viscosity ratio may not be favorable. It is also found that processing temperature leads to a higher electrical conductivity in the respective blends. Dielectric measurements reveal the existence of metallic type of conduction in the co-continuous compositions as the permittivity could not be measured in the low frequency range. However, 80/20 blends show low ε' value which is frequency independent.

Overall, it is observed that CB particles essentially influence the type of morphology of PP/ABS blends and the dispersion of CB particles determine the extent of conductivity in PP/ABS+CB composites.

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