Melt-Mixed Polypropylene/Acrylonitrile-Butadiene-Styrene Blends with Multiwall Carbon Nanotubes: Effect of Compatibilizer and Modifier on Morphology and Electrical Conductivity

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ABSTRACT: Cocontinuous blends of 45/55 polypropylene (PP)/acrylonitrile-butadiene-styrene (ABS) with multiwall carbon nanotubes (MWNT) were prepared by melt-mixing in a conical twin-screw microcompounder. PP-*grafted*-maleic anhydride (PP-*g*-MA) and styrene MA were used as compatibilizers for PP/ABS blends. Scanning electron microscopic observations showed phase segregation of PP-*g*-MA in the blends. State of dispersion of MWNT in the presence or absence of the compatibilizers was assessed through AC electrical conductivity measurements and crystallization studies of the blends. An improvement in AC electrical conductivity was observed in blends in presence of either styrene MA or dual compatibilizers. The lowest electrical percolation threshold was achieved at 0.1 wt % of MWNT using sodium salt of 6-amino hexanoic acid-modified MWNT. Significant increase in crystallization temperature of PP phase of blends with MWNT was observed in the presence of compatibilizers as compared to blends without compatibilizers. An attempt has been made to address the complex issues of phase segregation, compatibilization, and dispersion of MWNT in cocontinuous blends of PP/ABS. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2663–2672, 2011

Key words: blends; multiwall carbon nanotubes; electrical conductivity; morphology; polypropylene (PP)

INTRODUCTION

Blending of two or more polymers is a versatile tool to achieve the materials with enhanced properties, if properly compatibilized. Despite having adequate mechanical properties and excellent chemical resistance, one of the shortcomings of polypropylene (PP) is low impact strength, which can be improved by the use of rubbery polymers, viz., ethylene-propylene-diene monomer and acrylonitrile-butadiene-styrene (ABS).[1] These blends are inherently immiscible and incompatible. However, for structural applications, at least partial compatibility between the blend components is desired.[2] PP/ABS blends are inherently immiscible and incompatible, exhibiting coarse morphology.[3] Several studies investigated the effect of various compatibilizers, viz., ethylene vinyl acetate, PP-*grafted*-maleic anhydride (PP-*g*-MA), PP-*grafted*-acrylic acid, PP-*grafted*-2-hydroxy ethyl methacrylate, and PP-*grafted*-styrene acrylonitrile (PP-*g*-SAN), on morphology and impact properties of PP/ABS blends.[4–6] However, most of them were found to act as effective compatibilizers only in blends with PP-rich phase.[6] In this context, the use of more than one compatibilizer has also been investigated.[7–9]

Although most of the research in PP/ABS blends is focused on the improvement in mechanical properties, the bulk electrical conductivity of the blends in the presence of conducting filler, viz., carbon black or carbon nanotubes, has not received much attention. Carbon nanotubes have been exploited as a suitable candidate because of their excellent electrical properties and exceptionally good mechanical properties, replacing the conventional fillers like carbon blacks, metallic fillers, and carbon fibers.[10] However, the existence of strong intertube van der Waals forces leads to higher electrical percolation threshold as compared to theoretically predicted percolation threshold, calculated on the basis of aspect ratio of the nanotubes. Blending of different polymers not only provides the material with desired properties but also an efficient way to reduce the percolation threshold using the concept of "double percolation."[11,12] Dispersion of conducting fillers in polymer blends is governed by the

surface free-energy differences between the polymer and the filler, melt viscosity ratio of the blends, and kinetic parameters involved during melt-mixing.

Various strategies such as covalent and noncovalent functionalization of multiwall carbon nanotubes (MWNT) have been used to improve the dispersion and interfacial adhesion of MWNT with polymer matrix. Specific interactions such as "cation-π" type of interaction has also been proven successful in achieving better dispersion of MWNT, which leads to lower electrical percolation thresholds.[13–15]

The work undertaken here addresses the issues concerning the state of dispersion of MWNT in PP/ABS blends. An attempt has been made to improve the dispersion of MWNT by introducing polar groups-containing polymers, e.g., PP-g-MA and styrene MA (SMA) copolymer, which can also act as a compatibilizer in PP/ABS blends. Further, MWNT were modified with a unique modifier (sodium salt of 6-amino hexanoic acid, Na-AHA). It is expected that the melt interfacial reaction between MA functionality of PP-g-MA or SMA and the amine functional group of Na-AHA will facilitate improved dispersion of MWNT. A systematic investigation has been carried out in PP/ABS blends with MWNT to investigate the role of modifier (Na-AHA) and the compatibilizers (PP-g-MA and SMA) on the morphology and electrical conductivity of the blends. Crystallization studies have also been carried out to investigate the influence of MWNT along with modifier and compatibilizer on the crystallization behavior of PP.

EXPERIMENTAL

Materials and specimen preparation

PP (H200MA, melt flow index (MFI) 23, at 230°C with a load of 2.16 kg) was obtained from Reliance Industries Ltd., India. ABS copolymer (Absolac-120, with composition as: acrylonitrile 24 wt %, styrene 59.5 wt %, and rubber content 16.5 wt %) was

TABLE I
Properties of Different Grades of PP-g-MA

PP-g-MA designation	Maleic anhydride content (wt %)	MFI (190°C, 2.16 kg)
X	0.24	153
Y	0.45	48
G	0.9	14

obtained from Bayer India Ltd. PP-g-MA was supplied by Pluss Polymers Pvt. Ltd., New Delhi, India. Table I depicts the characteristic properties of various grades of PP-g-MA used in this study. SMA copolymers of 8% MA (Dylark 232, SMA8) and of 14% MA (Dylark 332, SMA14) were supplied by Nova Chemicals. Catalytic chemical vapor deposition-synthesized MWNT were obtained from Nanocyl CA, Belgium (NC-3100, average length: 1.5 μm, average diameter: 9.5 nm, purity > 95%).

PP/ABS blends in the presence or absence of MWNT were prepared by melt-mixing in a conical twin-screw microcompounder (Micro 5, DSM Research, the Netherlands) at 260°C with a rotational speed of 150 rpm. All blend components were pre-dried in vacuum oven at 80°C for at least 24 h. In blends with MWNT, PP and MWNT were melt-mixed for 10 min followed by the addition of ABS for 5 min. In case of PP-g-MA-compatibilized blends, PP-g-MA (5 wt %) was melt-mixed with PP and MWNT for 10 min followed by the addition of ABS. In case of SMA-compatibilized blends, PP and MWNT were melt-mixed for 10 min followed by the addition of SMA (5 wt %) and ABS. For dual compatibilized blends, initially PP-g-MA (2.5 wt %, with MA content 0.9 wt %) was melt-mixed with PP and MWNT followed by the addition of SMA (2.5 wt %) and ABS. Table II describes the codes and description of all the blend samples.

Na-AHA-modified MWNT were prepared as per procedure described earlier.[13] Compatibilized and uncompatibilized PP/ABS blends with Na-AHA-

TABLE II
Codes and Compositions of PP/ABS Blends

Codes	Compositions
Neat	45/55 PP/ABS blends
Tx	45/55 PP/ABS blend with x wt % of p-MWNT
MyTx	45/55 PP/ABS blend with x wt % of Na-AHA-modified MWNT (p-MWNT : Na-AHA ratio, 1 : y)
G5Tx	45/55 PP/ABS blend with PP-g-MA (5 wt %) and x wt % of p-MWNT
S5Tx	45/55 PP/ABS blend with SMA (5 wt %) and x wt % of p-MWNT
Dual Tx	45/55 PP/ABS blend with dual compatibilizers (5 wt %) and x wt % of p-MWNT
G5MyTx	45/55 PP/ABS blend with PP-g-MA (5 wt %) and x wt % of Na-AHA-modified MWNT (p-MWNT : Na-AHA ratio, 1 : y)
S5MyTx	45/55 PP/ABS blend with SMA (5 wt %) and x wt % of Na-AHA-modified MWNT (p-MWNT : Na-AHA ratio, 1 : y)
Dual MyTx	45/55 PP/ABS blend with dual compatibilizers (5 wt %) and x wt % of Na-AHA-modified MWNT (p-MWNT : Na-AHA ratio, 1 : y)

modified MWNT were prepared in a similar sequence mentioned for blends with unmodified MWNT. Injection-molded samples (according to ASTM D 638, Type V) were prepared using mini-injection molding machine from DSM Research. 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

Scanning electron microscopy

PP/ABS blends morphology and state of dispersion of MWNT in blends were studied through scanning electron microscopic (SEM) analysis. Extrudate strands were cryofractured in liquid nitrogen and selectively etched in tetrahydrofuran for removing ABS. The etched surface was gold sputtered to avoid the charging of the sample. These samples were then observed under SEM using Hitachi S3400N.

AC electrical conductivity

AC electrical 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).

Differential scanning calorimetry

Differential scanning calorimetry measurements were carried out using a DSC Q10 from TA instruments. The extruded samples of about 5 mg were dried in a vacuum oven before experiment. The samples were melted at 260°C and were kept for 3 min to delete the thermal history. Samples were then cooled to −20°C at a rate of 10 K/min, and crystallization exotherms were recorded. Following this, samples were again heated to 260°C at a heating rate of 10 K/min wherein melting endotherms for samples were recorded. All the thermal runs were carried out in nitrogen atmosphere. Temperature and transition heat were calibrated with indium standard. The degree of crystallinity of PP phase was calculated from the heat of fusion of second heating run. The heat of fusion (ΔH_m) of PP phase was normalized to the fraction of PP present in the composites. The degree of crystallinity (X_c) of PP phase was determined from the ratio of normalized heat of fusion ($\Delta H_{m,\text{norm}}$) to the heat of fusion of 100% crystalline PP, $(\Delta H_m)_0$, which was taken as 207.1 J/g.[16]

RESULTS AND DISCUSSION

Morphological analysis of compatibilized blends

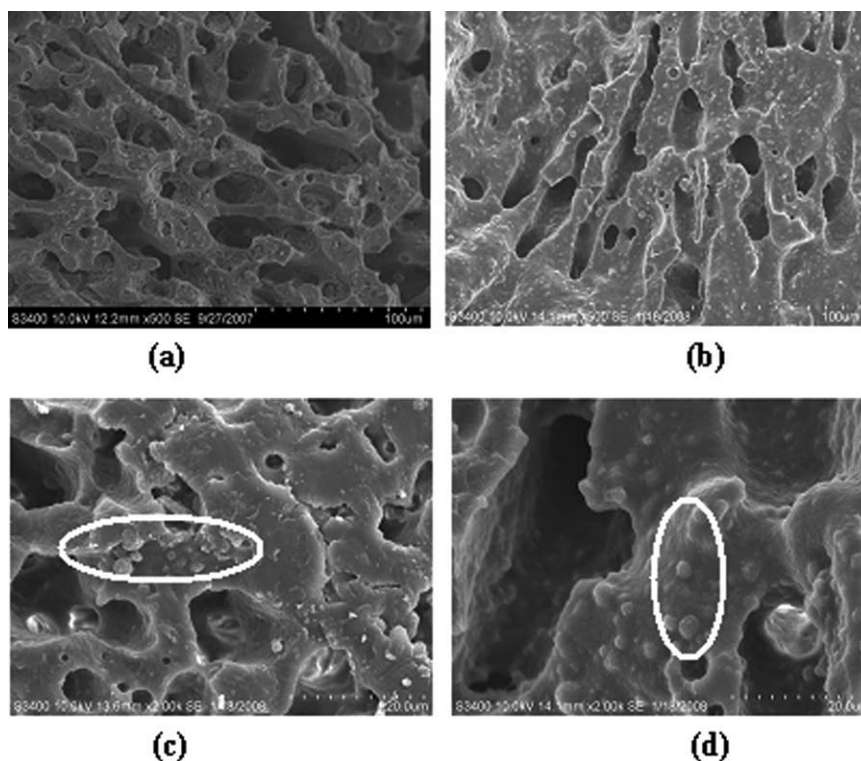Figure 1 shows the SEM micrographs of cryofractured and etched surfaces of 45/55 PP/ABS blends

Figure 1 SEM micrographs of 45/55 PP/ABS blends with 5 wt % PP-g-MA (a) PP/ABS, (b) PP/ABS/G (scale bar: 100 μm) and higher magnification images of (c) PP/ABS/X and (d) PP/ABS/Y (scale bar: 20 μm).
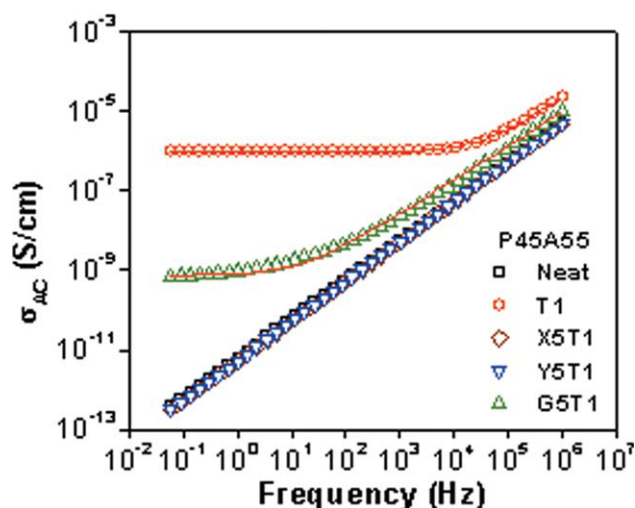
Figure 2 Effect of different MFI of PP-*g*-MA (5 wt %) on bulk electrical conductivity of PP/ABS blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compatibilized with commercially available three different grades of PP-*g*-MA. It is observed that the coarse cocontinuous morphology associated with 45/55 PP/ABS blends does not exhibit refinement on incorporation of various grades of PP-*g*-MA [Fig. 1(a–b)]. These blends rather depict phase-segregated domains of PP-*g*-MA near the interphase as well as in the bulk. The observed phase segregation of PP-*g*-MA could be due to very large difference in the melt viscosities of PP and PP-*g*-MA. Earlier studies on PP/ABS blends have also reported a similar phase segregation of the compatibilizer, PP-*g*-acrylic acid.[6] In case of composites, the lower viscosity of the segregating phase could facilitate the aggregation of fillers in the specific phase (PP-*g*-MA), which may alter the electrical percolation threshold.

Polarity-induced dispersion of MWNT in PP/ABS blends

The variation of electrical conductivity in co-continuous 45/55 PP/ABS blends in the presence of 1 wt % MWNT and compatibilized with various grades of PP-*g*-MA is presented in Figure 2. It is observed from Figure 2 that the electrical conductivity of the blends with PP-*g*-MA is lower than that of the blends without PP-*g*-MA. Moreover, PP/ABS blends with X (PP-*g*-MA with MFI = 153) and Y (PP-*g*-MA with MFI = 48) are insulating. As addressed earlier, presumably, the lower melt viscosities of X and Y resulted in the phase segregation of PP-*g*-MA in the blends. Such phase segregation along with the possibility of wetting of MWNT is presumably the reason behind the decrease in the AC electrical conductivity of the blends. It is to be noted that significantly lower electrical percolation threshold (0.4–0.5 wt %)

could be achieved in co-continuous 45/55 PP/ABS blends through the conceptual implementation of double percolation phenomenon wherein MWNT were observed to localize predominantly in less-viscous PP phase.[17] Nonpolar nature of PP further helps in forming three-dimensional percolating "network-like" structure of MWNT predominantly through "filler–filler" interaction. In this context, the addition of PP-*g*-MA may lead to a better dispersion of MWNT in the PP matrix; however, "matrix–filler" interaction dominates over "filler–filler" interaction in presence of PP-*g*-MA, which may lead to a breakdown of "network-like" structure of MWNT and higher percolation threshold. Addition of PP-*g*-MA in PP-based composites has been reported to show improved dispersion of silica in PP/silica composites.[18] State of dispersion in such composites depends predominantly on the amount of PP-*g*-MA and more specifically on the amount of grafted MA present.

To improve MWNT dispersion, a second compatibilizer was used wherein, SMA (5 wt %) was added instead of PP-*g*-MA in 45/55 PP/ABS blends with MWNT. It was considered that higher MA content of SMA (8% and 14%) as compared to PP-*g*-MA (0.9 wt %) would help in further improvement in dispersion of MWNT. It was expected that styrene part of SMA would be miscible with ABS phase of
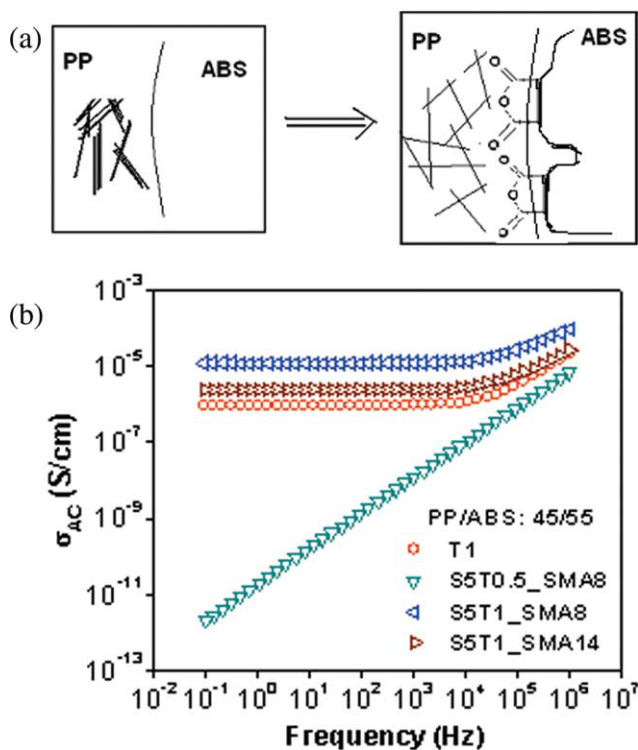

Figure 3 (a) Schematic showing the possible interaction of SMA with MWNT. (b) AC electrical conductivity of 45/55 PP/ABS blends compatibilized with SMA (5 wt %) in the presence of MWNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
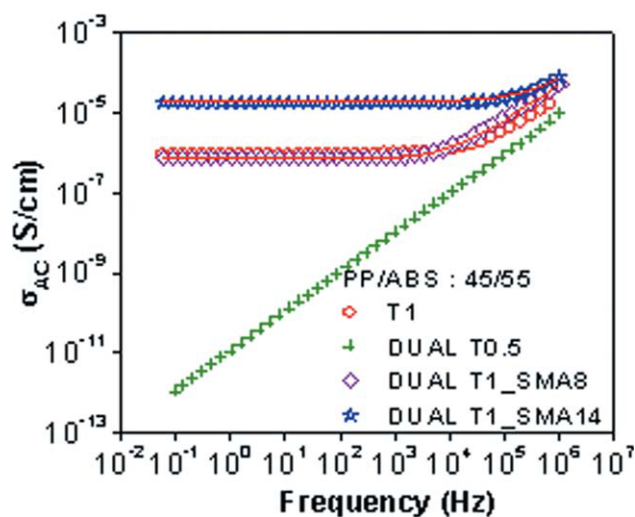
Figure 4 AC electrical conductivity of 45/55 PP/ABS blends with dual compatibilizers (PP-g-MA + SMA) in the presence of MWNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

blends, and MA would possibly aid in dispersion of MWNT. Figure 3(a) describes the schematic of the possible interaction between SMA and MWNT in PP/ABS blends. In addition to this, styrenic copolymer like SMA has also been reported to compatibilize PP/ABS blends.[19] Figure 3(b) exhibits the variation of electrical conductivity of 45/55 PP/ABS blends with SMA8 and SMA14 in the presence of MWNT. The electrical conductivity of the blends with SMA8 in the presence of 0.5 wt % MWNT is observed to be lower than corresponding blends without SMA. Further, an enhancement in the bulk electrical conductivity over two orders of magnitude is observed in case of SMA8-compatibilized PP/ABS blends with 1 wt % MWNT. The increase in electrical conductivity in SMA14-based composition is marginally lower compared with SMA8-based blends. It is well reported in the literature that the lower electrical conductivity in the compatibilized blends at percolation threshold could be because of the increased interfacial area after compatibilization and part of the tubes may reside at the interface.[20] Further, above percolation threshold, the improvement of the AC electrical conductivity is associated with the formation of refined "network-like" structure of MWNT.

In this context, further investigation has been carried out using a combination of PP-g-MA (2.5 wt %) and SMA (2.5 wt %) as a compatibilizer in 45/55 PP/ABS blends. It is worth mentioning here that PP-g-MA and SMA are observed to act as effective compatibilizers for PP/ABS blends in which PP and ABS are major phases in the blends, respectively. Thus, an additional advantage of using the dual components in combination may arise on the fact that it can offer compatibilization of PP/ABS blends over a wide range of compo-

sitions. Figure 4 exhibits the effect of such dual compatibilizers on the electrical conductivity of the 45/55 PP/ABS blends with MWNT. An increase in the bulk electrical conductivity by about three orders of magnitude compared with PP-g-MA compatibilized blends is observed with dual compatibilizers. However, blends with 0.5 wt % MWNT still exhibit insulating behavior presumably because of the phase segregation or changes in the interfacial area.

Morphology and electrical conductivity of PP/ABS blends with MWNT in the presence of PP-g-MA and SMA

Figure 5 exhibits the AC electrical conductivity and SEM micrographs of 45/55 PP/ABS blends with 1 wt % MWNT in the presence of various compatibilizers. It is evident from the figure that addition of a single compatibilizer or dual compatibilizers has significant influence on the electrical conductivity of PP/ABS blends. An improvement in AC electrical conductivity of blends is observed with SMA and with dual compatibilizers, whereas drastic reduction in electrical conductivity is observed in blends with PP-g-MA. Morphological observation of these blends is likely to elucidate the results regarding AC electrical conductivity data in detail. Figure 5(b–f) shows SEM micrographs of the PP/ABS blends with MWNT and with different compatibilizers. Figure 5(b) exhibits the SEM micrograph of 45/55 PP/ABS neat blends (in the absence of any compatibilizer or MWNT). Cocontinuous morphology with subinclusions of ABS phase in PP ligaments is evident here. As observed from Figure 5(c), MWNT do not show any prominent effect on the morphology of blends. It is worth mentioning that a reduction in ligament thickness of 45/55 PP/ABS blends in the presence of 5 wt % of MWNT has been observed earlier.[17] Further, as seen from Figure 5(d), PP-g-MA exhibits no significant effect on the morphology of 45/55 PP/ABS blends. However, a significant decrease in the electrical conductivity is observed in the presence of PP-g-MA. This is presumably because of the phase segregation of PP-g-MA as observed in Figure 5(e). Further, in Figure 5(e), various hierarchical structures connected by MWNT are evident in the PP phase. Moreover, the circled portion shows the phase-segregated domain of PP-g-MA in the PP phase. Interestingly, a refinement in the morphology [Fig. 5(f)] along with improved electrical conductivity is observed in blends with dual compatibilizers. The refinement in the morphology is likely to be associated with the concentrations of the compatibilizers chosen (2.5 wt % PP-g-MA and 2.5 wt % SMA), which is probably well below the critical micelle concentration in which the phase segregation could not be possible. Overall, the 45/55 PP/ABS blends with dual compatibilizers exhibit refinement in the
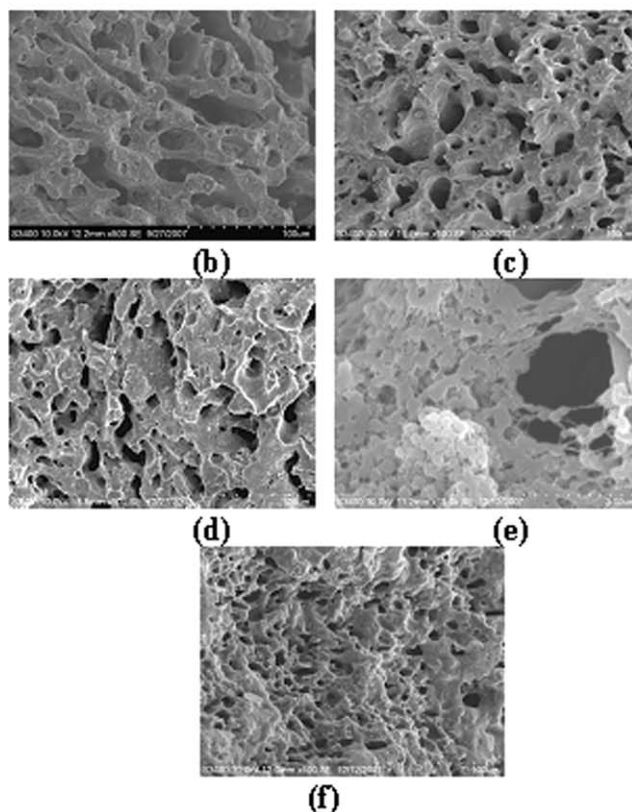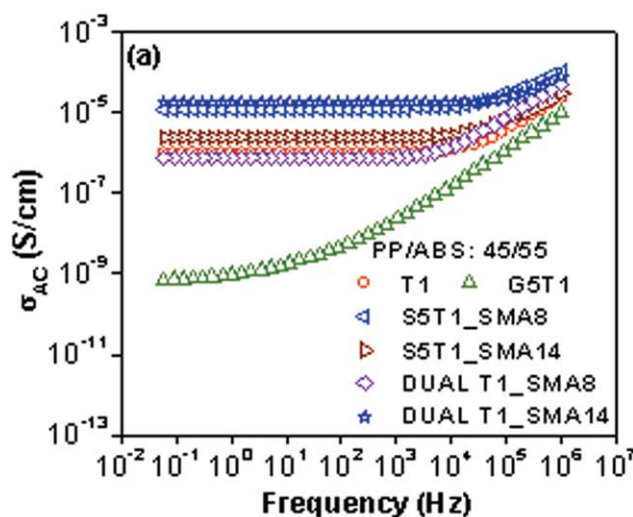
Figure 5 (a) AC electrical conductivity of PP/ABS blends with various compatibilizers and MWNT. SEM micrographs of (b) 45/55 PP/ABS blends, (c) P45T1A55, (d) P45G5T1A55, and higher magnification image of (e) P45G5T1A55 and (f) dual T1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

morphology and better electrical conductivity as compared to blends with PP-g-MA.

Controlling the dispersion of MWNT through specific interactions in PP/ABS blends with PP-g-MA and SMA

It is well established that the strong intertube van der Waals forces often tend to form agglomerates

of MWNT, making homogeneous dispersion a challenge. In this context, the concept of "cation-π" interaction has been proven successful in PA6 and its blend with ABS. In this context, MWNT were also modified with Na-AHA as described in the earlier reports.[6,7]

Figure 6(a) depicts the variation in electrical conductivity with frequency for PP/ABS (45/55) blends with unmodified as well Na-AHA-modified MWNT. As seen from the figure, blends with unmodified MWNT exhibit insulating behavior up to 0.4 wt % MWNT. Electrical percolation threshold is found to be observed between 0.4 and 0.5 wt % MWNT. Interestingly, modifying MWNT with Na-AHA has resulted in decrease in the electrical percolation threshold of the blends. 45/55 PP/ABS blends containing only 0.1 wt % of modified MWNT exhibit higher electrical conductivity compared with blends containing 0.5 wt % of unmodified MWNT.
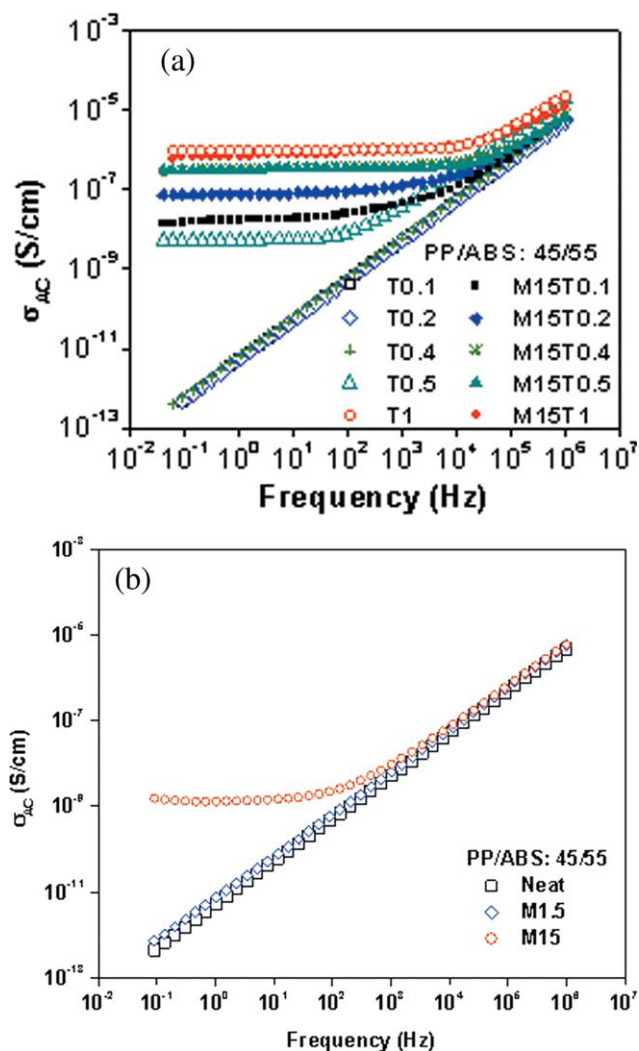

Figure 6 (a) Effect of Na-AHA-modified MWNT (MWNT : Na-AHA = 1 : 15) on AC electrical conductivity of PP/ABS blends (45/55). (b) Effect of Na-AHA on electrical conductivity of PP/ABS blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, only marginal improvement in the conductivity is observed above 0.4 wt % Na-AHA modified MWNT.

In this context, the contribution of Na^+ ionic moieties of the modifier (Na-AHA) toward the electrical conductivity of the blends has been studied for the blends with Na-AHA only. These blends were prepared in a similar way, i.e., 10 min melt-mixing of PP with Na-AHA followed by the addition of ABS. The lowest Na-AHA content in the studied system was 1.5 wt % and the highest concentration was 15 wt %. Hence, these two specific compositions were selected for the analysis. It is observed from Figure 6(b) that blends containing 1.5 wt % Na-AHA exhibit insulating nature, whereas blends with 15 wt % modifier show the conductivity of about 10^{-9} S/cm. However, 45/55 PP/ABS blends with Na-AHA-modified MWNT (0.1 wt %) exhibit a DC electrical conductivity of $\sim 10^{-8}$ S/cm. Thus, the lower percolation threshold (~ 0.1 wt %) associated with modified MWNT is perhaps related to the refinement of the "network-like" structure of MWNT in the presence of the modifier.

It is envisaged that amine functional group of Na-AHA may undergo melt interfacial reaction with MA functionality of the compatibilizer and may lead to the restriction of MWNT in the PP phase. Figure 7(a) depicts the AC electrical conductivity of PP-g-MA-compatibilized PP/ABS blends with Na-AHA-modified MWNT of various ratios of MWNT : Na-AHA. A progressive increase in the electrical conductivity is observed with the increasing Na-AHA content at fixed MWNT concentration (1 wt %) in the PP/ABS blends. An increase in three orders of magnitude is observed at 1 wt % modified MWNT (MWNT : Na-AHA, 1 : 15) in PP-g-MA-compatibilized PP/ABS blends. Besides "cation-π" type of interaction, use of Na-AHA facilitates in restricting the MWNT in PP phase because of melt interfacial reaction between amine group of Na-AHA and MA group of PP-g-MA.[21] Such synergistic effect made it possible to achieve an increase in the bulk electrical conductivity in case of PP-g-MA-compatibilized blends.

However, a different behavior has been observed with modified MWNT in case of dual compatibilized blends [Fig. 7(b)]. A decrease in two to three orders of magnitude in the bulk electrical conductivity is evident in case of dual compatibilized blends. In case of Na-AHA-modified MWNT, possibility of reaction between -NH_2 group of modifier and MA functionality of SMA may lead to distribution of MWNT even in the ABS phase, deviating from the concept of double percolation. Further, melt-interfacial reaction is expected to be more in case of SMA with higher MA content. As a result, the electrical conductivity is observed to be much lower in case of dual compatibilized blend containing SMA14.
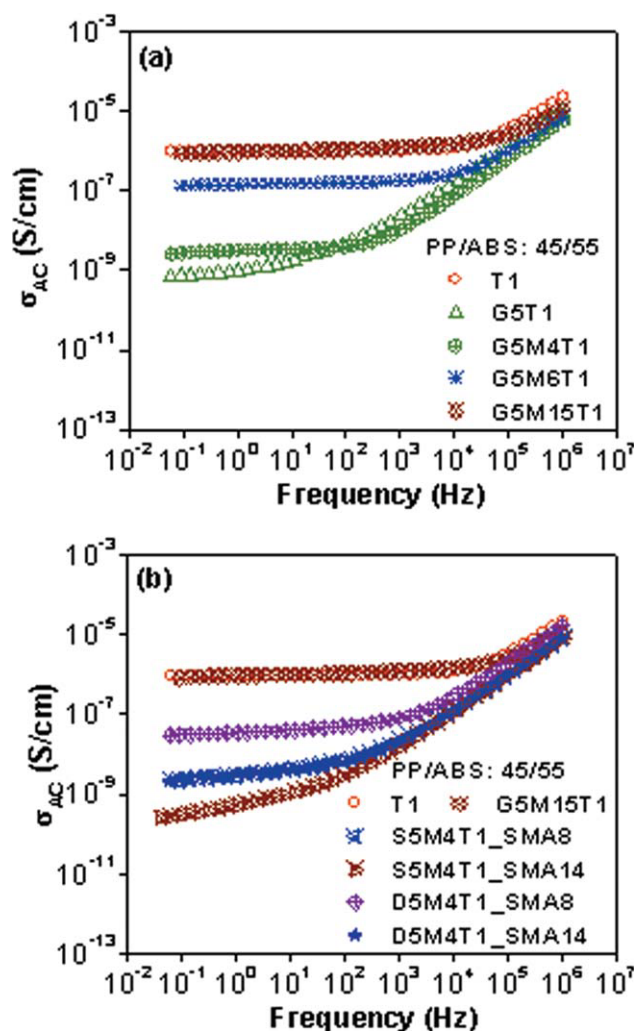

Figure 7 Effect of modified MWNT on bulk electrical conductivity of PP/ABS blends with (a) PP-g-MA-compatibilized blends with various ratios of MWNT : Na-AHA (at 1 wt % MWNT) and (b) SMA and dual-compatibilized blends with 1 wt % MWNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Further, the electrical conductivity of the blends is reduced drastically [Fig. 7(b)] when only SMA was used as the compatibilizer. Because only SMA was used, all amine groups of Na-AHA-modified MWNT had the probability to react with MA functionality of SMA. As a result, a large fraction of MWNT content may possibly migrate to the ABS phase. Thus, much lower electrical conductivity is observed in SMA-compatibilized blends with modified MWNT. The conductivity was observed to be lower in the case of SMA14-compatibilized as compared to blends with SMA8. It is worth pointing out here that the possible encapsulation of MWNT by reaction mass of amine group of Na-AHA and MA functionality of SMA may also be the reason behind such decreased electrical conductivity. Such reactions between MA functionality and amine group
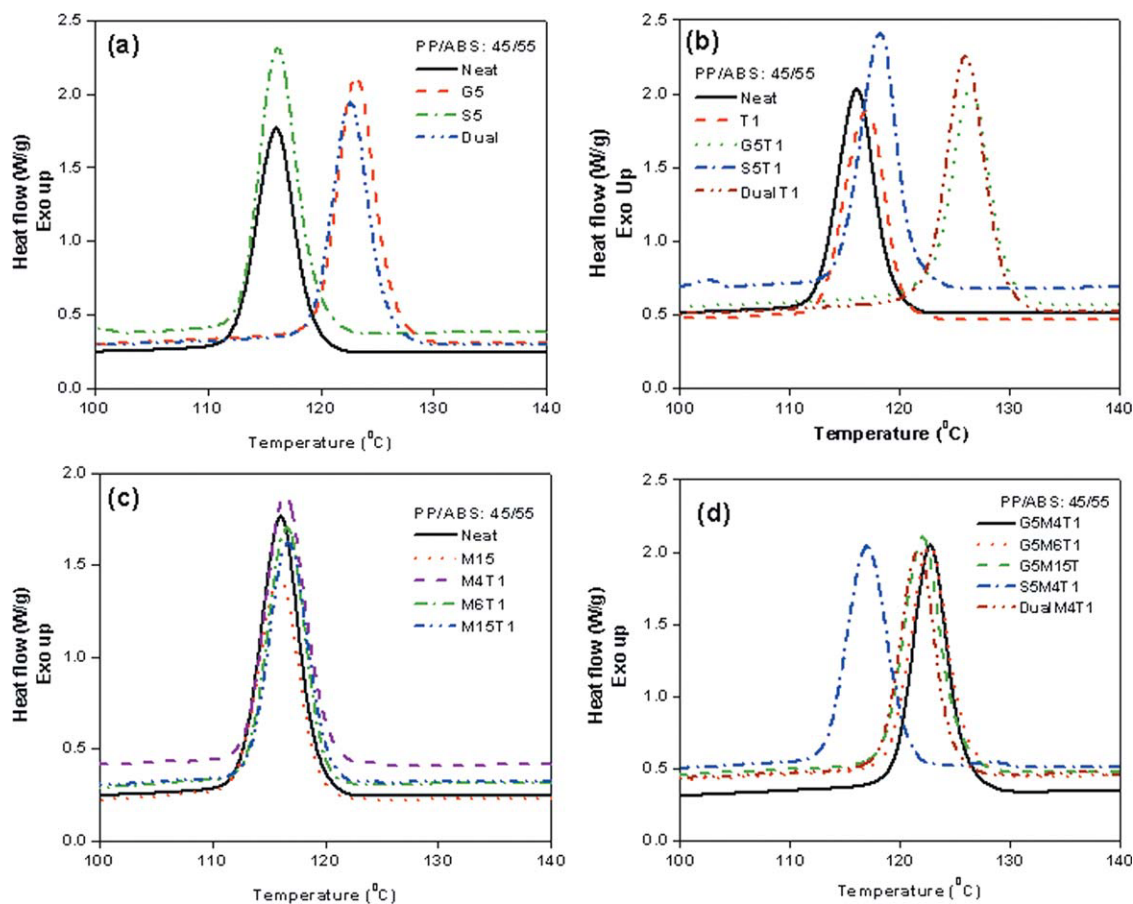
Figure 8 Differential scanning calorimetry crystallization exotherms for 45/55 PP/ABS blends with (a) various compatibilizers, (b) various compatibilizers along with MWNT, (c) with Na-AHA-modified MWNT, and (d) various compatibilizers along with Na-AHA-modified MWNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are well established and confirmed through Fourier transform infrared spectroscopy analysis.[22]

Role of PP-g-MA and SMA on crystallization behavior of PP/ABS blends with MWNT

The crystallization exotherms for 45/55 PP/ABS blends in the presence of either PP-g-MA or SMA or dual compatibilizers are depicted in Figure 8(a). Addition of PP-g-MA exhibits a nucleating effect on PP, resulting in an increase in the onset and peak crystallization temperature (T_c) [Fig. 8(a)]. PP and PP-g-MA are observed to crystallize at the same temperature in all blend samples. Nucleating ability of PP-g-MA in PP/PP-g-MA composites has already been reported in the literature.[18] SMA is observed to show no prominent changes in the crystallization temperature of PP. T_c for dual compatibilized blends is observed to be slightly lower compared with PP-g-MA compatibilized blends. Further, addition of PP-g-MA is observed to manifest in an increase in the degree of crystallinity of the blends. Table III summarizes the crystallization parameters of these blends.

Figure 8(b) exhibits the crystallization exotherms for compatibilized PP/ABS blends in the presence of MWNT. PP/ABS blends with 1 wt % MWNT results in a slight increase in the T_c of PP, suggesting the heterogeneous nucleating action of MWNT. However, significant increase in the T_c is observed in case of blends with PP-g-MA, SMA, or dual compatibilizers with MWNT. This essentially indicates the finer dispersion of MWNT, leading to higher number of heterogeneous nucleating sites available for crystallization of PP in blends containing polar components, viz., PP-g-MA, SMA, or dual compatibilizers.

Figure 8(c) exhibits the crystallization exotherms for 45/55 PP/ABS blends with Na-AHA-modified MWNT of varying ratios of MWNT : Na-AHA (1 : 4, 1 : 6, and 1 : 15). Variation in the MWNT : Na-AHA ratio does not result in any appreciable change in crystallization temperature of PP. Blends with 15 wt % Na-AHA do not exhibit any significant effect on crystallization temperature of PP in blends.

Figure 8(d) exhibits the crystallization exotherms of compatibilized PP/ABS blends with Na-AHA-modified MWNT. Interestingly, crystallization temperature

TABLE III
Melting and Crystallization Properties of PP/ABS Blends with MWNT in the
Presence of PP-g-MA, SMA, and Dual Compatibilizers

Composition	T_c (°C)	T_m (°C)	H_m (J/g)	Degree of crystallinity (%)	FWHM (°C)
PP	113.8	159.5	100.5	48.5	4.23
P45A55	116.08	159.1	39.6	42.5	3.19
T1	117.0	158.7	36.3	39.4	3.51
G5	123.1	161.6	48.5	54.8	3.15
S5	116.2	159.4	41.0	46.3	3.23
Dual	122.7	161.4	42.4	47.9	3.0
G5T1	126.5	162.5	41.0	46.8	3.27
S5T1	118.2	159.6	42.3	48.3	3.18
Dual T1	126.0	162.7	46.7	53.3	3.3
M15	116.0	159.8	39.6	50.0	3.43
M4T1	116.5	159.5	45.9	51.9	3.41
M6T1	116.6	159.1	33.7	38.9	3.2
M15T1	116.7	159.4	32.5	41.5	3.32
G5M4T1	122.7	161.6	53.6	63.9	3.1
G5M6T1	122.7	161.5	50.5	61.6	3.4
G5M15T1	122.0	161.2	51.1	69.4	3.31
S5M4T1	116.9	159.6	50.1	59.8	3.53
Dual M4T1	121.7	161.3	47.0	56.1	3.04

is observed to be lower for compatibilized blends with Na-AHA-modified MWNT as compared to blends with corresponding composition but with unmodified MWNT. This is presumably due to inability of Na-AHA-modified MWNT to act as nucleating agent in the presence of compatibilizers. Presumably, the encapsulation of MWNT in the presence of compatibilizer and modifier could be one of the reasons for suppressing the heteronucleating action of MWNT. Similar observation has been reported for PA6/SWNT composites, wherein SWNT were modified with SMA.[22] Further, in case of blends with PP-g-MA and modified MWNT, varying the ratio of MWNT : Na-AHA (1 : 4 to 1 : 15) does not result in any significant change in crystallization temperature. Further, in case of blends containing SMA (alone or in combination with PP-g-MA in dual compatibilizers), the possibility of migration of modified MWNT to ABS phase as a consequence of reaction between -NH$_2$ group of modifier and anhydride groups of SMA may result in a decrease in the number of heterogeneous nucleating sites available in the PP phase. Such decrease in density of heterogeneous nucleating agents available in PP phase may also be one of the reasons for decrease in crystallization temperature of PP in the blends.

Except blends containing PP-g-MA, all blends exhibit relatively same melting temperature of ~160°C. Slightly higher melting temperature, ~162°C, is observed for blends containing PP-g-MA. Na-AHA and SMA are observed to show no prominent effect on melting temperature of PP in PP/ABS blends. Full width at half maximum measurements of the crystallization peaks revealed that the full width at half maximum is nearly constant, indicating that crystal size distribution is not affected with the addition of compatibilizer and modifier.

CONCLUSIONS

The role of single or dual compatibilizers, viz., PP-g-MA and SMA, in governing the dispersion of MWNT in 45/55 PP/ABS blends has been extensively studied through morphology, electrical conductivity, and crystallization studies. Further, uniform dispersion and debundling of MWNT was achieved through the use of a unique modifier (Na-AHA) using the concept of specific interaction. The lowest electrical percolation was achieved at 0.1 wt % of MWNT using Na-AHA-modified MWNT. MWNT were observed to act as heterogeneous nucleating agents for PP. Improved dispersion resulted in a significant improvement in AC electrical conductivity and nucleating ability of MWNT. Encapsulation of MWNT and migration to other phase was observed to reduce the heteronucleating action of MWNT.

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