<Original Paper>

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Effect of Introduction of Terminal Functions on Properties of Multi-walled Carbon Nanotube/*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene CompositesTakahide KUMAGAI*, Wataru SUZUKI*, Eisuke YAMADA*,
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Abstract

The effects of interfacial adhesion between multi-walled carbon nanotubes (MWCNTs) and terminal-functionalized polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene (SEBS) matrices have been investigated by determining the mechanical properties of these composites. SEBS with no functionalization (SEBS-1) and SEBSs functionalized by carboxylic acid group (SEBS-3), amino group (SEBS-4), and maleic acid anhydride groups on the middle block (SEBS-2) were used. The nanocomposites were prepared by using a roll mill. The tensile properties and electric conductivity of all the composites improved with increasing MWCNT content. In the SEBS-4 composite system, the tensile moduli were almost three times higher than those of pure SEBS-4 with 17.8 vol% of MWCNT. Further, the electric percolation threshold of CNT/SEBS-4 was higher than that of the others; this indicates that the terminal amino group significantly contributes to the interfacial adhesion, even when the content of the terminals is relatively low. In mechanical analysis of the composites, a broad loss tangent peak appeared at the temperature region between the glass transition point of the mid-block and the polystyrene block. These results suggest that a stereoscopic network structure is formed by the loading of MWCNTs.

Key words : carbon nanotube, styrene block copolymer, terminal function, interfacial adhesion, nanocomposite

1. Introduction

The effects of the terminal functions of polymer chains on the properties of polymers, even with relatively low total quantities, and their adhesiveness to

other materials often vary widely because the adhesion force is affected by various factors such as elasticity, viscosity, wettability, and compatibility of polymers to the adherend. As a result, the terminal functions make the phase structures and the polarities of polymers to change drastically^{1~5)}.

Furthermore, multi-walled carbon nanotubes (MWCNTs) have good mechanical properties, heat resistance, and electric properties⁶⁾, and they have been investigated for applications to many industrial fields^{7~11)}. In particular, their applications to the nanocomposite technology to realize materials having high performance and functionality by combining nanofillers and polymer matrices have attracted the interest of many researchers^{12, 13)}. One of the most successful developments

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in recent times is the sealant of the elastomer composite used in oil-drilling equipment¹¹⁾, which has to be stable at higher temperatures and pressures. Endo et al. have suggested that the rubber composites with MWCNTs should be reinforced not only by "bound rubber," which is the conventional filler-reinforcement model, but also by the formation of a novel three-dimensional structure using MWCNTs. The reinforcement mechanism seems to be affected by an interfacial adhesion between an elastomer matrix and MWCNT in the former case, and by the physical nature of the CNTs, including size and dispersibility, in the latter case. Therefore, when MWCNTs are combined with elastomer matrices, CNT-polymer interfacial binding, or adhesiveness, is the important parameter.

MWCNTs for applications to CNT-polymer nanocomposites have been investigated by researchers previously and have recently been manufactured by the chemical vapor deposition (CVD) method. This is because MWCNTs are suitable for mass production, and its surface activity is high (similar to carbon black¹⁴⁾; in other words, their adhesiveness to polymers is good. However, the surface activity makes CNTs agglomerate with other tubes and form strong bundle structures, leading to poorer dispersibility. Hence, researchers have devoted considerable effort to improve their compatibility with polymers¹⁵⁾ or dispersibility into matrices¹⁶⁾. On the other hand, MWCNTs with graphitized surfaces (g-MWCNT) have a lower surface activity than the other tubes, while their dispersibility and electrical conductivity are superior^{11, 14)}. In addition, in a previous study, we have demonstrated that the g-MWCNT/SBS composites exhibit better mechanical properties¹⁴⁾ due to the above-mentioned reinforcing mechanism.

In this report, we present investigations into the adhesion of main-chain-functionalized and terminal functionalized elastomer matrices to g-MWCNTs carbon nanotubes. We have aimed to establish a method for further improving the mechanical properties of the g-MWCNT/thermoplastic elastomer composite and achieving a good balance between its electrical and mechanical properties. Polystyrene-*block*-poly(ethylene-co-butylene)-*block*-polystyrene (SEBS), which has a wide variety of industrial applications today, for example, in plastic parts, automotive interiors, films, sealants, and resin modifier, is used as the polymer matrix. In

the case of the functionalized SEBS, maleic acid anhydrides were grafted on the middle block and carboxyl or primary amino groups were introduced at the terminals of chains. Further, the effects of the introduction of the functions into the SEBSs on the mechanical and electrical properties have been reported.

2. Experimental

2.1 Materials

All the elastomer matrices used in this study were supplied by Asahi Kasei Chemicals. We used polystyrene-*block*-poly(ethylene-co-butylene)-*block*-polystyrene with a number-averaged molecular weight (M_n) of 50,000 and polystyrene (PS) weight fraction of 30 wt%, which from here onward is called SEBS-1. SEBS with maleic acid anhydride grafted on its middle block, SEBS-2, had M_n of 50,000; its maleic acid anhydride content was ~2 wt% and the PS weight fraction was 30 wt%. A carboxyl or a primary amino-terminated SEBS, SEBS-3 or SEBS-4, respectively, had M_n of 52,000; the contents of the terminal functions were ~0.2 wt% and the PS weight fraction was 30 wt%. Commercially available g-MWCNT (g-MWCNT, VGCF-S) from Showa Denko K. K. with diameters ranging from 80-100 nm, average lengths of 10 μ m, surface oxygen amount of 2.1 atm% (determined by XPS), and the G/D ratio of 9.09 were employed.

2.2 Preparation of samples

SEBS-1, SEBS-2, SEBS-3, and SEBS-4 (50 g each) were milled using a six-inch open roll, and subsequently, 5 to 25 g of g-MWCNT (~18 vol%) was mixed into the SEBSs at room temperature. Each composite was then pressed for 10 min at 150 °C to a thickness of approximately 1 mm. Isothermal annealing of the composites was carried out by heating them in an oven for 24 h at 100 °C under vacuum and cooling slowly to room temperature. Finally, the samples were cut to a suitable shape for subsequent measurements.

2.3 Measurement of samples

Tensile tests were conducted according to Japan Industrial Standards (JIS) K6251 at room temperature with a testing machine (RTA-100, Orientec Co., Ltd., Tokyo, Japan); the shape was ISO Type1A, and the thickness was approximately 1 mm. Electrical resistivity measurements were conducted according to JIS K6911

and JIS K7194 for more and less than $10^6 \Omega$, respectively; the shape was a square of approximately 50 mm. Dynamic viscoelastic behaviors including the storage modulus (E') and loss modulus (E'') were detected by a dynamic mechanical analyzer (Q-800, TA Instruments, Inc., New Castle, DE) in the tensile mode. Temperature scans were conducted at a heating rate of $5^\circ\text{C}/\text{min}$ from -100 to 300°C with a fixed measurement frequency of 1 Hz.

3. Results and Discussion

3.1 Tensile properties

In the case of filler-elastomer composites, 100% and 300% elongation strengths (M_{100} and M_{300} , respectively) have typically been used to measure the reinforcement efficiency due to the addition of fillers. This is because the adhesivity between a filler and matrix is closely related to their reinforcement. Hence, the interfacial adhesion can be directly observed as a drag (or a stress) against the composite deformation, which is partly because a decrease in the molecular mobility by the filler surface constrains the polymer chains¹⁷⁾. Table 1 shows the tensile properties including tensile strength (T_B), elongation at break (E_B), M_{100} , and M_{300} of the investigated nanocomposites. Further, the relationship between the rate of change of M_{100} and M_{300} and the volume fraction of g-MWCNT is shown in Fig. 1 in order to clarify the differences in the effects of the introduction of the functional groups in greater detail, since the pristine SEBSs have different tensile property values.

In the case of the SEBS-1 composite systems, at 17.8

Table 1 Tensile properties of g-MWCNT/SEBSs composites.

Matrix	ϕ_F / vol%	M_{100} / MPa	M_{300} / MPa	T_B / MPa	E_B / %
SEBS-1	0.0	3.2	5.3	33.8	510
	2.1	3.3	5.3	28.7	510
	4.2	3.7	6.6	33.6	520
	8.0	4.1	7.1	22.3	510
	11.5	4.5	8.0	20.7	505
	14.8	4.9	9.0	19.8	490
SEBS-2	17.8	5.3	9.6	20.3	500
	0.0	3.2	5.9	33.0	570
	2.1	3.3	5.3	23.9	580
	4.2	4.3	6.2	22.5	560
	8.1	4.7	6.9	19.5	565
	11.6	6.1	8.4	19.1	530
SEBS-3	14.9	7.2	9.7	18.5	520
	18.0	8.4	10.7	15.7	460
	0.0	3.9	7.0	40.5	510
	2.1	3.8	7.7	34.1	505
	4.2	4.5	8.1	32.6	510
	8.0	5.4	10.6	26.7	500
SEBS-4	11.5	6.3	10.5	24.3	550
	14.8	7.2	12.8	29.5	565
	17.8	8.2	13.0	24.7	535
	0.0	3.7	6.8	36.7	535
	2.1	3.9	7.3	34.1	530
	4.2	4.1	8.1	32.1	530
SEBS-4	8.0	5.8	10.4	22.8	465
	11.5	6.7	12.2	28.3	530
	14.8	8.3	15.2	22.6	430
	17.8	10.7	17.5	24.7	455

vol% of CNT concentration, M_{100} increased with g-MWCNT and was reached in approximately half the time that required for pure SEBS-1. Further, the change in M_{300} was similar to that in M_{100} . The rate of increase of SEBS-2 (with grafted maleic acid anhydrides on the middle blocks) was greater than that of SEBS-1. M_{100} of the composites at 18.0 vol% of g-MWCNT loading was nearly 2.5-fold more than that of pristine SEBS-2. However, the rate of increase of M_{300} was smaller than that of SEBS-1. Similarly, both the matrices having the terminal functions were more reinforced by the addition of g-MWCNT than SEBS-1; in particular, M_{100} of the SEBS-4 composite was nearly three times higher at 17.8 vol% of g-MWCNT than M_{100} of pure SEBS-4. In contrast, the reinforcing effect in the case of M_{300} of SEBS-4 composites was the highest among all the SEBSs composites. T_B of all the investigated samples tends to decrease with increasing g-MWCNT concentrations, but the rates of decline of both SEBS-3 and SEBS-4 were slightly lower than that of SEBS-1.

These results indicate that the improvement in the interfacial adhesion between g-MWCNT and matrix by the introduction of the terminal amino group into SEBS is equivalent to or better than the improvement

Fig. 1 Relationships between the changes in tensile moduli and volume fraction of g-MWCNT of the composites.

obtained by grafting maleic anhydride into the middle chain of the SEBS, even when the introduced amounts of the terminal group were relatively small.

3.2 Hansen solubility parameter

The improvement in the adhesion as a result of the introduction of carboxyl or amino groups can be qualitatively explained based on the concept of the Hansen solubility parameter (HSP)¹⁸⁾. Solubility, which results from the interaction between molecules, is closely related to adhesive properties. The advantage of the HSP concept is its wide range of applicability; in fact, HSP has been used to assess the dispersibility of nanofillers¹⁸⁾. The HSP parameters including δ_D , δ_P , and δ_H of g-MWCNT were determined as 21.3, 3.9, and 7.2, respectively, from a preliminary research using 20 organic solvents. In this study, we have evaluated the compatibility between g-MWCNT and each SEBS by employing the calculated HSP values of g-MWCNT and the related component of the matrices. Table 2 shows the HSP parameters of each component. In addition, the table lists the relative energy difference (RED) as an affinity parameter that has been calculated using Eqs. (1) and (2) as follows:

$$(R_a)^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \quad (1)$$
$$RED = R_a / R_0 \quad (2)$$

Here, R_0 is the interaction criteria; R_a , the solubility parameter distance; and the subscripts 1 and 2, the solute (the surface of the g-MWCNT) and solvent (the matrices), respectively.

The surface of tubes was graphitized highly, but δ_P and δ_H of g-MWCNT are larger than 0, indicating that there are some functions causing the hydrophilicity of g-MWCNT on the surface. Moreover, the presence of a few oxygen atoms has been verified by XPS. Therefore, a small portion of the g-MWCNT surface has been oxidized, which will show slight acidity.

The RED of both the terminal-functionalized PS

Table 2 Hansen solubility parameters, δ_D , δ_P and δ_H , of g-MWCNT, PS, carboxylic-terminated PS, and amino-terminated PS, respectively, and each relative energy difference (RED) for g-MWCNT.

	$\delta_D / \text{MPa}^{1/2}$	$\delta_P / \text{MPa}^{1/2}$	$\delta_H / \text{MPa}^{1/2}$	RED
g-MWCNT	21.3	3.9	7.2	-
Poly(ethylene- <i>co</i> -butylene)	16.9	3.4	0.3	1.65
Polystyrene	18.5	4.5	2.9	1.04
Carboxylic-terminated PS	19.1	5.0	8.2	0.68
Amino-terminated PS	19.0	4.9	6.1	0.71

blocks is lower than pure PS blocks, which indicates that the compatibility of these blocks with the surface is higher than those of the other components. However, HSP parameter values were calculated based on the combination of one of the function groups per styrene unit; the actual values of δ_P and δ_H would be smaller than the values shown in the table. In any case, these results qualitatively indicate that the compatibility and adhesiveness of terminal-functionalized SEBS to g-MWCNT is higher than those of pristine SEBS. In addition, the reinforcing effect of SEBS-4 system (amino-terminal) is higher than that of SEBS-3 system (carboxyl-terminal), whereas both of RED values are subequal. This may be due to the acid-base interaction between the surface of g-MWCNT and terminal amino groups of SEBS-4.

3.3 Electric resistivity

When the volume fraction of fillers with electric conductivity, such as carbon black, is above a critical limit, the electrical resistance of the composites decreases sharply; this phenomenon is referred to as percolation. This phenomenon occurs because the fillers form an interconnecting network from end to end in a matrix. MWCNTs have excellent electric conductivity and the conductive network is formed more easily than in the case of carbon black¹⁴⁾.

Fig. 2 shows the relationship between the volume resistivity (ρ_v) of the SEBS composites and the vol-

Fig. 2 Relationships between volume resistivity and volume fraction of g-MWCNT of the composites.

ume fraction of the g-MWCNT. From this figure, it is evident that the resistivities of SEBS-1 and SEBS-3 composites decrease drastically at 2.1 vol%, and further, they decrease gradually to 17.8 vol%. These results indicate that percolation thresholds are present up to 2.1 vol% for the two matrices. On the other hand, SEBS-2 and SEBS-4 composites exhibit drastic decreases at 4.2 vol%, which suggests that a percolation threshold exists between 2.1–4.2 vol% in these systems. These results reveal that the greater adhesion between amino groups and g-MWCNTs has an undesired effect on the electrical conductivity at a smaller loading range. However, the resistivities of all the composites decreased to almost the same level as the g-MWCNT concentration was increased. Finally, the resistivities decreased to almost one-tenth of that of seawater.

The effect on the electric resistivity of the composites is based on two phenomena. First, it is related to the adhesiveness between g-MWCNT and SEBSs at lower concentrations. The polymer matrices become a bound polymer on the surface as an electric insulator¹⁹⁾ and behave like an electric resistance. Further, the compatibility of SEBS-4 with g-MWCNT is higher than that of the other SEBSs, leading to increasing insulator amounts and electric resistance. However, this does not hold true at higher concentrations, and the effect can be attributed to certain three-dimensional structures formed by the combination of MWCNTs and matrices; this is similar to the results of Thongprachan et al²⁰⁾. Thus, at higher concentrations, the highly structured CNT-elastomer networks are considered to behave not as individual or clustered networks but as one unified structure. During the process of forming structures, the entropy of this system increases as the network grows; consequently, a driving force for contact between g-MWCNTs is generated. Because this driving force eliminates the insulator layers through g-MWCNTs, at high CNT loading, the electrical resistivities of each composite will be in the same range as those when there is no increase in resistivity due to bound polymer formation.

3.4 Dynamic viscoelastic behavior

The basic parameters of dynamic viscoelasticity, including E' and E'' , change significantly with temperature, reflecting the process of phase transition of polymer matrices. In particular, for the viscoelastic

behavior of SEBS, which is a typical block copolymer, the relaxation behaviors of the soft block and rigid PS phase clearly appeared at the temperature in the measured range. In addition, in the composites involving rigid materials such as inorganic fillers, their E' increased, which reflects the higher elastic modulus of the fillers.

Fig. 3~6 show the temperature dependences of E' , E'' , and $\tan \delta$ of the g-MWCNT composites, respectively. For E' of pristine SEBSs, there are two drastic drops at around -40°C and 100°C due to the glass transitions of the middle chain and PS block, respectively, indicating the definite phase separation between poly(ethylene-co-butylene) (PEB) and PS phase.

In SEBS-1 systems, the E' values increased with g-MWCNT loading over the entire temperature range. The E' slope at the primary decreasing region changed into a two-step descent above 11.5 vol%. SEBS-3 and SEBS-4 also showed the same tendency as SEBS-1; however, the increasing rates of both the terminal-functionalized SEBSs are higher than that of SEBS-1. These results are consistent with the results of the tensile test, which indicates that the interfacial interactions between the CNT-matrixes are also reflected in the dynamic properties of composites. Moreover, the E' values of all the composites above the temperature region of 130°C increased, resulting in the prevention of thermal softening of matrices.

All the temperature dispersions of E'' of pristine SEBSs have two peaks at regions from -40 to -30°C and from 90 to 100°C . These peaks as well as the results of E' reflect the relaxation phenomena arising from glass transitions of PEB and PS phases, respectively. It is noteworthy that a clear shoulder-shaped relaxation appears in the range from 0 to 20°C for the CNT fraction of 17.8 vol% only in the case of the SEBS-3 and SEBS-4 composites.

Assuming that the maxima of the temperature dependences of $\tan \delta$ were glass transition points (T_g), the peak values of T_{gEB} and T_{gS} of the PEB and PS phases, respectively, are shown in Table 3. T_{gEB} values of the pristine SEBS-3 and -4 are lower while T_{gS} values are higher than those of SEBS-1. These differences can be attributed to the stronger tendency of phase-separation structure in the two SEBSs having terminal functions as a result of the effect of the hydrogen-bonding interactions between the terminal-functional

Fig. 3 Temperature dependences of E' , E'' , and $\tan \delta$ of g-MWCNT/SEBS-1 composites.

Fig. 5 Temperature dependences of E' , E'' , and $\tan \delta$ of g-MWCNT/SEBS-3 composites.

Fig. 4 Temperature dependences of E' , E'' , and $\tan \delta$ of g-MWCNT/SEBS-2 composites.

Fig. 6 Temperature dependences of E' , E'' , and $\tan \delta$ of g-MWCNT/SEBS-4 composites.

Table 3 T_g of PEB phase and PS domain of g-MWCNT/SEBSs composites determined by $\tan \delta$ curves, and the peak values.

Matrix	ϕ_f / vol%	$T_{gH} / ^\circ\text{C}$	Peak value	$T_{gS} / ^\circ\text{C}$	Peak value
SEBS-1	0.0	-25.9	0.28	114.9	0.49
	4.2	-25.0	0.25	122.7	0.49
	8.0	-24.5	0.27	122.0	0.45
	11.5	-20.3	0.24	121.0	0.42
	14.8	-18.2	0.22	121.6	0.42
SEBS-2	0.0	-21.4	0.27	117.4	0.41
	4.2	-22.7	0.25	120.0	0.44
	8.1	-20.8	0.26	121.2	0.41
	11.6	-17.7	0.22	122.3	0.39
	14.9	-17.4	0.20	122.0	0.40
SEBS-3	0.0	-34.1	0.28	118.2	0.50
	4.2	-32.4	0.27	122.9	0.45
	8.0	-31.6	0.27	123.5	0.44
	11.5	-29.9	0.22	124.2	0.47
	14.8	-28.5	0.19	123.7	0.47
SEBS-4	0.0	-36.2	0.24	119.4	0.64
	4.2	-34.5	0.25	122.5	0.50
	8.0	-33.8	0.28	122.8	0.44
	11.5	-30.6	0.22	123.4	0.48
	14.8	-30.4	0.18	123.4	0.47
	17.8	-31.8	0.17	123.3	0.49

groups. T_{gS} values of SEBS-3 and -4 increase with the g-MWCNT content, and they are higher than those of the other systems. This is because the PS chains having terminal functional groups formed an interaction layer on the g-MWCNT surfaces, and hence, the mobility of the polymer chains decreased to less than those of the others. These results indicate that the driving force for forming the interfacial interaction layer between g-MWCNTs and SEBS matrices is the compatibility of the terminal functions with the CNT surface.

The above-mentioned novel relaxation phenomena in the temperature range from 0 to 20 °C for the temperature dependence of E'' were similarly reflected between 0 and 50 °C in the curves of $\tan \delta$ (E''/E'); in particular, a distinct peak appeared in the same temperature region for the SEBS-4 composite. This can be attributed to the formation of three-dimensional structures by the loading of the MWCNTs into the elastomer matrix, and it agrees with the work of Noguchi et al.²¹⁾ The difference in the formation of the unique CNT structure can be evaluated semi-quantitatively using $\tan \delta$ as the viscoelastic parameters because the peak area is related to the number of units that are relaxed at the corresponding temperature. The $\tan \delta$ values of all the CNT composites at the temperature range from 0 to 100 °C are larger than those of the pristine SEBSs. These results are in agreement with the experimental results of Noguchi et al., wherein CNTs formed an internal structure in the MWCNT composite. Although the $\tan \delta$ values of the entire composites with CNT loading of 17.8 vol% are more than 0.2, those of SEBS-4 are higher than those of the others; the broad peak appears in the same temperature range. In other words, the highly grown internal structure is formed

primarily in the SEBS-4 matrix in this study. Therefore, the results of the dynamic viscoelastic behavior indicate that the introduction of functional groups to relatively scarce terminals not only improves adhesivity with g-MWCNT and mechanical properties, but also encourages the formation of the three-dimensional structures due to their adhesive force.

4. Conclusion

In this paper, the tensile properties, electric resistivities, and dynamic viscoelasticities of the composites prepared by combining terminal-functionalized SEBSs and graphitized MWCNTs have been investigated.

The tensile properties of the composites prepared from SEBSs with terminal functions were significantly improved as compared to those of the pristine SEBS composites because the interfacial adhesions between SEBSs and g-MWCNT increased due to the introduction of functional groups to the terminals of these matrices. Further, the improvement in the amino-terminal SEBS was higher than that in the maleic anhydride-grafted SEBS, even when the introduced amount of the terminal groups was relatively few. The compatibility between the g-MWCNT surface and SEBSs, that is, the interaction strength, could be explained qualitatively using the concept of HSP and RED as an affinity parameter.

In the case of the conductivity of composites, the greater adhesion between SEBS-4 and g-MWCNT surfaces led to undesired results because of the formation of bound polymers that act as an insulator. However, when the CNT concentration was greater than 14.8 vol%, highly structured CNT-elastomer networks were formed in the composites, resulting in higher conductivity.

The results of a dynamic mechanical analysis of the composites indicate the formation of three-dimensional networks by a combination of g-MWCNTs and SEBSs. The $\tan \delta$ curve of the SEBS-4 composite exhibits a stronger relaxation, which suggests that the introduction of the amino group accelerates the formation of the network structures more than the other modifications.

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<研究論文>

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多層カーボンナノチューブ／ポリスチレン-*block*-ポリ(エチレン-*co*-ブチレン)-*block*-ポリスチレン複合物の諸物性に対する末端官能基の影響

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要 旨

多層カーボンナノチューブ (MWCNT) と末端修飾ポリスチレン-*block*-ポリ(エチレン-*co*-ブチレン)-*block*-ポリスチレン (SEBS) との複合物を調製し、それらの材料間の界面接着の効果が機械的物性に及ぼす影響を検討した。母材として、未修飾 SEBS (SEBS-1)、および末端カルボキシル基修飾 SEBS (SEBS-3)、末端アミノ基修飾 SEBS (SEBS-4) および中鎖無水マレイン酸修飾 SEBS (SEBS-2) を用いた。複合物は、二本ロールを用いて調製した。17.8 vol% の SEBS-4 複合物の引張モジュラスは、その無添加物の約三倍にまで増加した。MWCNT/SEBS-4 の電気伝導度のパーコレーション閾値は、他と比較して高かった。これらの結果は、末端官能基が比較的小さい量であるにもかかわらず、末端アミノ基が界面接着性に寄与していることを示唆する。

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