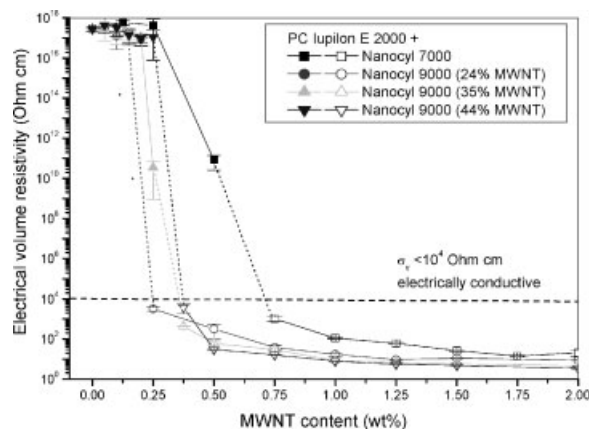


A Novel Strategy to Incorporate Carbon Nanotubes into Thermoplastic Matrices^a

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Multiwalled carbon nanotubes (MWNT) are introduced into thermoplastic matrices (polycarbonate and polyamide) by melt blending using polyethylene (PE) based concentrates with high MWNT loadings (24–44 wt.-%). MWNT surfaces were treated with a metallocene-based complex to afford the in-situ polymerization of ethylene directly from the surface. The resulting concentrates showed excellent MWNT pre-dispersion. Due to the high interfacial energy between MWNT and PE, the nanotubes migrate into matrix polymers with lower interfacial energies, like polycarbonate and polyamide, and thereby remain in their excellent dispersion state. Thus, electrical percolation is achieved at lower MWNT contents as compared to direct incorporation. For polycarbonate it is shifted from 0.75 to 0.25 wt.-%.



Introduction

The effective use of carbon nanotubes (CNT) in composites with polymers requires excellent nanotube distribution and dispersion.^[1–8] However, nanotubes normally are produced in an agglomerated state (multiwalled carbon nanotubes, MWNT) or as bundles (single-walled carbon nanotubes, SWNT) with Van-der-Waals interactions between them. The direct incorporation of CNT powders

into thermoplastic matrices by melt mixing may result in agglomerates of nonwetted CNT in the composites (see example in^[8]). Such agglomerates reduce the fraction of CNT available for the formation of percolated pathways, but also act as imperfections in mechanical tests, thus reducing the potential of the nanotubes. Therefore, improvement of the dispersion of CNT is an important issue in current nanotube composite research.^[3–5,7]

Methods have been reported to synthesize polymer chains directly at the surface of nanofillers, like carbon nanotubes, thus, realising excellent wetting of the tubes by the polymer, separation of the tubes, and excellent dispersion in such concentrates. The method used is derived from the Polymerization-Filling-Technique (PFT) which initially was investigated in Ziegler-Natta polymerization and more recently was developed for metallocene catalysis and applied to a variety of microfillers, such as kaolin, silica, wollastonite and graphite.^[9]

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In the process, as developed by the group of Philippe Dubois at the University of Mons-Hainaut, Belgium, a nanotube pre-dispersion in polyethylene (PE) is achieved by a catalyzed in situ polymerization of ethylene directly from the nanotube surface which was treated with a metallocene-based complex. By this, PE chains grow from the surface of the MWNT leading to a coating and finally to a complete tube separation.^[9–11] Recently, based on these basic investigations, Nanocyl S.A. in Sambreville, Belgium, has developed the Nanocyl[®]9000 series. This series represents a unique additive that contains very high loading (up to 45 wt.-%) of MWNT already pre-dispersed in a high density PE carrier.^[12]

Another example is shown by the group of Walter Kaminsky at University of Hamburg, Germany, by in-situ polymerization of propylene with a metallocene/methylalumoxane catalyst on nanofillers like carbon nanotubes, carbon nanofibers, and carbon black.^[13,14]

In previous investigations it was demonstrated that nanocomposites prepared from PE concentrates with miscible (PE) and immiscible, but compatible polyolefin matrix materials (like ethylene vinylacetate, EVA), show enhanced nanotube dispersion and improved mechanical properties as compared to direct incorporation of the nanotubes.^[12]

It was the aim of this work to adapt the strategy of using concentrates of PE with excellent multiwalled carbon nanotube dispersion as carriers for the incorporation of MWNT into matrix polymers and apply this strategy also to materials which are highly immiscible with PE, like polycarbonate (PC) and polyamide (PA).

Experimental Part

Materials

Concentrates of high density PE synthesized as described above containing 24, 35, and 44 wt.-% MWNT (Nanocyl[®]9000 series) were incorporated into PC and polyamide 6 (PA6). The amount of MWNT in the concentrates was determined by TGA analysis. For comparison, pure nanotubes having the same dimensions as in the concentrates (Nanocyl[®]7000) were used. The average nanotube diameter was 9.5 nm, whereas the average length was 1.5 μm , the carbon purity was 90%, and the surface area was 250–300 $\text{m}^2 \cdot \text{g}^{-1}$ (see also homepage www.nanocyl.com). PC, Iupilon E 2000 powder (Mitsubishi Engineering Plastics, Japan) was used and was dry-mixed with the MWNT-PE concentrates before addition into the running compounder. As PA6 component, granules of Capron 8202 (BASF, Freeport, USA) were grounded to a powder before they were also premixed with the PE-MWNT concentrates.

Preparation

The melt mixing was performed using a DACA microcompounder (Daca Instruments, Goleta, USA) with a capacity of 4.5 cm^3 . This

microcompounder represents a conical twin screw extruder with a bypass, thus, allowing the material to circulate several times and to set rotation speed and mixing time independently. For PC the mixing conditions of 280 °C, 50 rpm, 15 min were selected, whereas for PA6 the temperature was set to 240 °C. The extruded strands were compression moulded at the processing temperatures to sheets with 60 mm diameter and 0.35 mm thickness in order to perform electrical measurements. Before each processing step the materials were dried; PC at 120 °C for 4 h under vacuum and PA6 at 80 °C, for 12 h under vacuum.

Electrical Characterization

The pressed plates were first measured using a 8009 Resistivity Fixture (ring electrodes with 60 mm diameter) equipped with a Keithley electrometer model 6517A designed for high resistivity samples (full symbols in the graphs of Figure 1). Samples, which showed resistivity values $<10^7 \Omega\text{cm}$ or could not be measured with this equipment, were investigated using a four-point test fixture combined with a Keithley electrometer model 2000 for which strips ($20 \times 3 \times 0.35 \text{ mm}^3$) were cut from the sheets (open symbols in the graphs of Figure 1). The values shown are mean values of 4 to 6 measurements.

Morphological Characterization

Scanning electron microscopy was performed on cryofractured surfaces of the pressed plates using a Philips XL30 microscope. Transmission electron microscopy was conducted on ultrathin sections cut at room temperature from the pressed plates (taken from a middle position) by means of a Zeiss EM 912 microscope (Zeiss, Germany). The microscope was adjusted with an acceleration voltage of 120 kV. The best contrast between filler and matrix was obtained by defocusing and use of a zero loss filter.

Results and Discussion

When comparing composites containing pure nanotubes with composites produced using the concentrates of PE with MWNT it is clearly seen that the electrical percolation concentration is shifted to lower values (Figure 1). In PC, the electrical percolation concentration was found as low as 0.25 wt.-% MWNT for the concentrate with 24 wt.-% MWNT, whereas for pure nanotube material having the same structural characteristic it occurred at 0.75 wt.-%. The concentrates having 35 and 44 wt.-% reached percolation at 0.375 wt.-%, whereas that with 35 wt.-% shows lower resistivity values at 0.25 and 0.375 wt.-%. At higher loadings, the concentrates with high MWNT content resulted in lower resistivity values.

For PA, the decrease in electrical volume resistivity versus the MWNT content occurs more gradual and not that steep like in PC which is assumed to be due to its partially crystalline structure. The resistivity values start

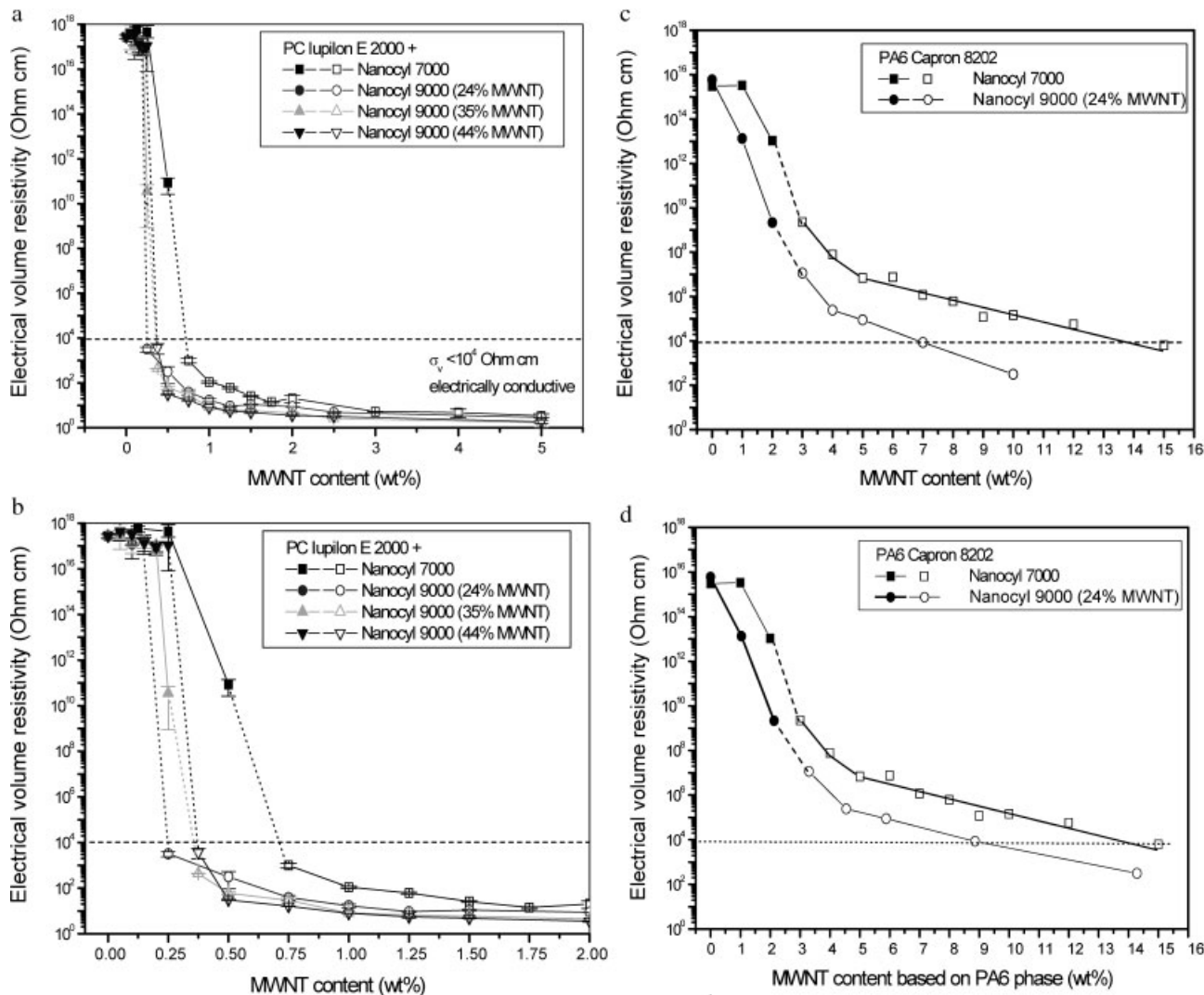


Figure 1. Electrical volume resistivity versus MWNT content comparing the use of pure MWNT material (Nanocyl[®] 7000) and MWNT concentrates in PE (Nanocyl[®] 9000 with different MWNT loadings); (a,b): in PC; (c,d): in PA6, c) versus MWNT content in the composite, d) versus MWNT content based on PA6 phase.

to decrease at 2 wt.-% for the pure nanotube material, whereas by incorporation via PE-MWNT concentrate containing 24 wt.-% MWNT this decrease starts already at 1 wt.-%. The values of resistivity are generally lower in the latter case. The resistivity value of $10^4 \Omega\text{cm}$, which serves as an upper limit for electrical conductive samples, is reached at 15 wt.-% for pure nanotubes, but at 7 wt.-% for incorporation via PE-MWNT concentrate. Assuming that all nanotubes are confined only in the matrix phase of the blend (as discussed later), the second phase reduces the content of this phase and, thus, the nanotube concentration in the matrix phase is higher than in the blend. This is considered in Figure 1d for the PA based blend composites, illustrating that the effect of lower percolation threshold and resistivity values by incorporation via PE-MWNT

concentrates is not just a blending/confinement effect. The same is true for PC as matrix (not shown).

By mixing concentrates of PE with MWNT to PC and PA6, blend structures consisting of base polymer matrix and small PE dispersed particles are formed as illustrated in Figure 2. The content of the PE component is linked to the nanotube content and is higher at increased nanotube loadings and lower concentration of the concentrates. At 0.25 wt.-% loading, the amount of PE in the blend composite is 0.79 wt.-% by using the concentrate with 24 wt.-% MWNT, but 0.32 wt.-% by using the concentrate with 44 wt.-% MWNT. The size of the PE particles in the PC matrix is in the range between 300 nm and 1.5 μm in case of the concentrate with 24 wt.-% MWNT and below 500 nm when using concentrates having 44 wt.-% MWNT. Thus,

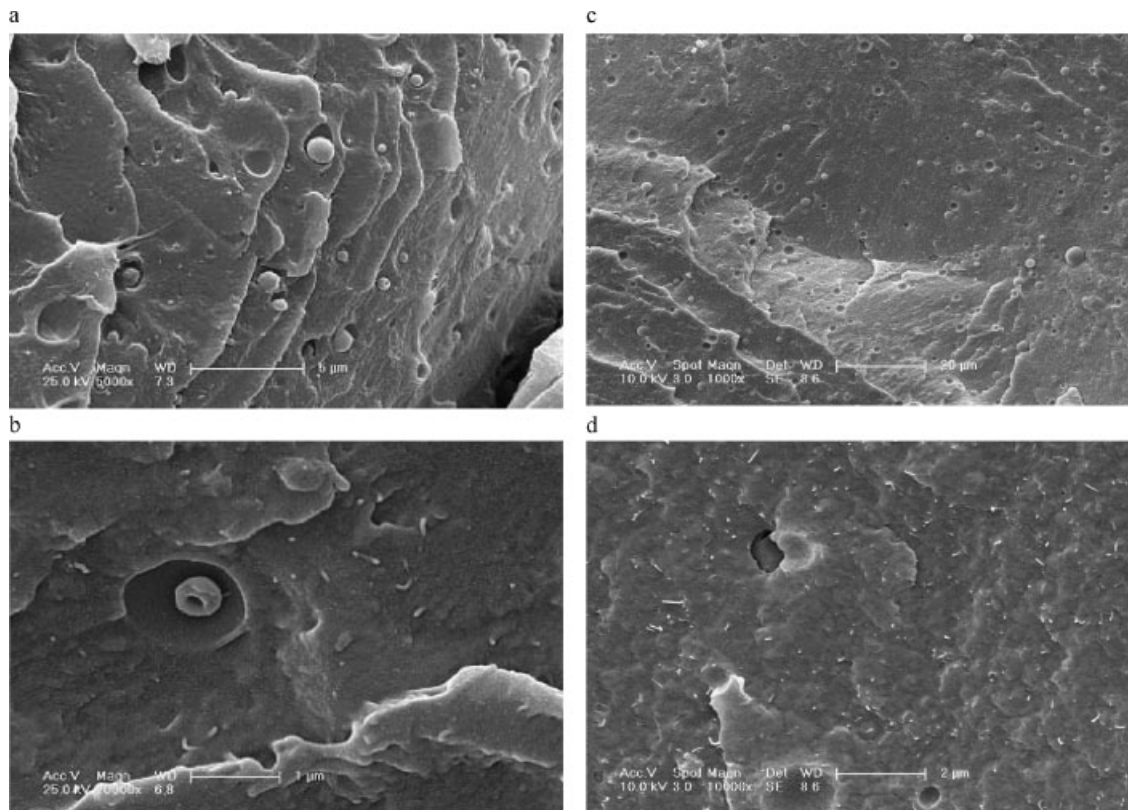


Figure 2. Scanning electron micrograph of cryofractured surfaces of blend composites; (a,b): based on PC containing 0.25 wt.-% MWNT, prepared from a PE concentrate with 24 wt.-% MWNT (a) and 44 wt.-% MWNT (b); (c,d): based on PA6 containing 1 wt.-% MWNT prepared from a PE concentrate with 24 wt.-% MWNT illustrating the blend structure (c) and the homogeneous dispersion of nanotubes in the PA matrix (d).

we may expect that such small particles do not disturb the matrix behaviour much.

In the PA6 matrix morphological studies were performed at 1 wt.-% where the amount of PE in the blend composite is 3.2 wt.-%. The particle size of the PE droplets is in the range between 1 and 5 μm with most of the particles having diameters of around 2 μm .

Interestingly, the nanotubes are found in majority to be migrated into the matrix materials (see Figure 2b,d) and only selected ones are partially covered by PE droplets. There are no nanotubes at the interface between PE and the matrix polymer. This may be also caused by the mismatch between the size of the dispersed PE droplets and the dimension (length) of the nanotubes.

The distribution of nanotubes within the polymer material is very homogeneous and the dispersion in both matrix materials is excellent, consisting of mainly individualized tubes as it was in the carrier PE material (see Figure 2b,d and 3). No agglomerates could be observed. On the other hand, electrical percolation is observed as illustrated by the measured resistivity values showing that there are at least some contacts (or small distances

within the hopping/tunnelling distance of electrons) between the nanotubes (which may be described as “agglomerated” and not “isolated” in an electrical sense).

These improvements can be explained as follow: Since PE is synthesized at the MWNT surface, the dispersion of MWNT within PE is excellent and all tubes are separated from each other by the grown polymer chains. Due to the way of the fixation of the catalyst on the nanotube surface, PE is adhered to the MWNT surface but it is not covalently bonded. During mixing of the PE-MWNT concentrate with the matrix polymer the typical processes of melt mixing occur. These include sheet like deformation of the lower melting minor PE component within the matrix polymer, formation of holes and a two-dimensional network of such sheets by reaching a critical thickness due to Raleigh instabilities, breaking of the PE melt structures into ribbons and fibers, and finally the formation of spherical droplets.^[15] Their size mainly depends on the interfacial energies between the matrix polymer and PE and on the viscosity ratios between these immiscible blend components. During these processes, a high surface area is continuously created which enables the migration of the

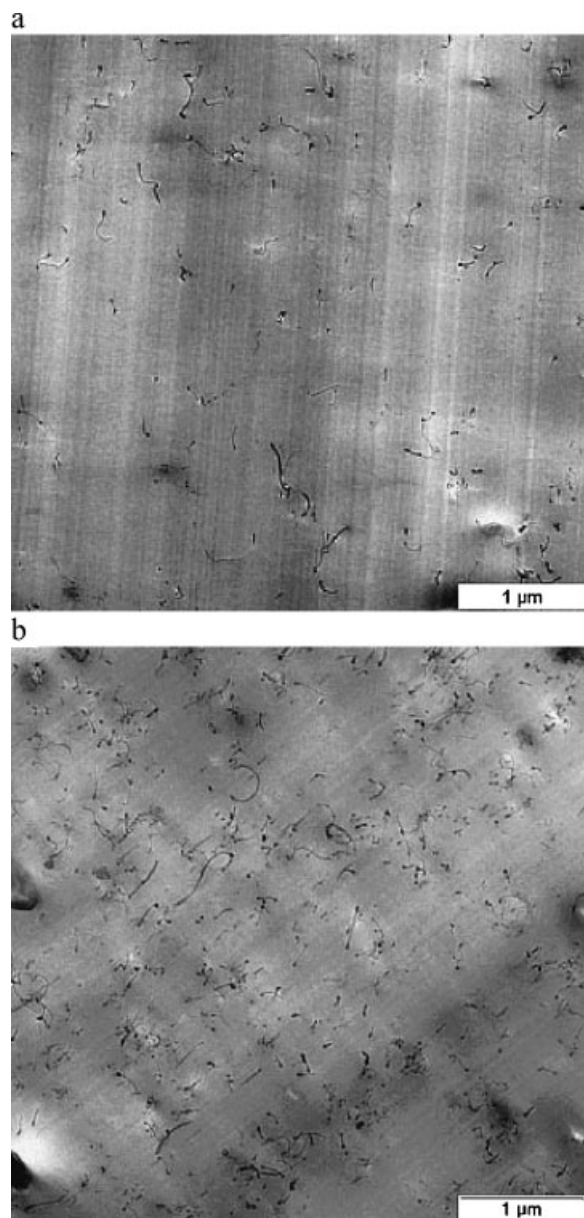


Figure 3. Transmission electron micrographs of thin sections of blend composites based on PC containing 0.25 wt.-% (a) and 1 wt.-% MWNT (b), prepared from a PE concentrate with 24 wt.-% MWNT illustrating the excellent dispersion of the nanotubes.

well dispersed nanotubes from the PE sheets, ribbons, fibers, and droplets towards the matrix polymer by remaining the excellent tube separation. The motivation for this migration lies in the much more favourable interaction between nanotubes and PA6 or PC than between nanotubes and PE.

This experimental finding can be supported by regarding the interfacial energies of the systems under consideration.

According to the Young's equation the location of a filler in an equilibrium state can be estimated by calculation of the wetting coefficient ω_a .^[16]

$$\omega_a = \frac{\sigma_{\text{CNT-B}} - \sigma_{\text{CNT-A}}}{\sigma_{\text{A-B}}} \quad (1)$$

with $\sigma_{\text{CNT-B}}$, interfacial energy between CNT and polymer component B; $\sigma_{\text{CNT-A}}$, interfacial energy between CNT and polymer component A; $\sigma_{\text{A-B}}$, interfacial energy between polymer components A and B.

If the wetting coefficient is higher than 1, the nanotubes are located in polymer A, when having values lower than -1 they are located in polymer B, and if the wetting coefficient is between 1 and -1 the nanotubes are preferentially located at the interface between both polymers.

The interfacial energy can be calculated from surface energies and their disperse and polar components. Mainly two approaches are used; namely the harmonic-mean and geometric-mean equations.^[17]

The harmonic-mean equation is commonly used to calculate the interfacial energy σ_{12} between polymer pairs:

$$\sigma_{12} = \sigma_1 + \sigma_2 - 4 \left[\frac{\sigma_1^d \sigma_2^d}{\sigma_1^d + \sigma_2^d} + \frac{\sigma_1^p \sigma_2^p}{\sigma_1^p + \sigma_2^p} \right] \quad (2)$$

with σ_1 , σ_2 surface energy of the components 1, 2; σ_1^d , σ_2^d disperse part of the surface energy of components 1, 2; σ_1^p , σ_2^p polar part of the surface energy of components 1, 2.

The geometric-mean equation is described in literature to be more suitable as compared to the harmonic mean equation for high surface energies^[17] (higher than $20 \text{ mJ} \cdot \text{m}^{-2}$, according to additional information from^[18]):

$$\sigma_{12} = \sigma_1 + \sigma_2 - 2 \left(\sqrt{\sigma_1^d \sigma_2^d} + \sqrt{\sigma_1^p \sigma_2^p} \right) \quad (3)$$

These equations were adapted to our systems. For multiwalled carbon nanotubes only limited knowledge exists concerning the surface energy and polarity. Nuriel et al.^[19] measured a surface energy value of $45.3 \text{ mJ} \cdot \text{m}^{-2}$ on MWNT having a slightly higher diameter ($30 \pm 15 \text{ nm}$) than the nanotubes used here. The polar free surface energy was measured from the contact angles towards polypropylene and PE glycol to be $26.9 \text{ mJ} \cdot \text{m}^{-2}$ leading to a polarity value of 59%.^[19] The finding of a relatively high polarity for carbon nanotubes is in agreement with measurements of Barber et al.^[20] who utilized atomic force microscopy and the Wilhelmy balance method to quantify the contact angle between nanotubes and a variety of organic liquids. They found for MWNT of 20 nm diameter, grown by an arc-discharge method, a polarity of 37%. For the estimation of interfacial tensions in

Table 1. Surface energies and polarities of the polymers and MWNT.

Material	Temperature	Surface energy ^{a)}	Polarity ^{b)}	Ref.
	°C	mJ · m ⁻²	%	
MWNT	–	45.3	59	[19]
PE	240	23.2	0	[18]
PE	280	20.9	0	[18]
PC	280	23.8	19.0	[18]
PA	240	32.2	30.1	[18]

^{a)}Calculated from surface tension values at 20 °C using the temperature coefficient; ^{b)}Calculated from values given in ref.^[18] at 20 °C, assuming temperature independency.

this paper the values from reference^[19] were used. In contrast to this relatively high filler polarity PE is completely nonpolar. The values of surface energies of the polymers at the appropriate temperatures were extrapolated from literature values^[17,18] and are shown in Table 1.

Even if the extrapolation of surface energies towards the melt state and the assumed temperature independence of polymer polarity are only first approximations these values can be used for an estimation of the interfacial energies σ_{12} between the components in our blend composites.

The calculated interfacial energies between the polymer pairs and between the nanotubes and the three polymers are shown in Table 2. It is clearly seen that the polymers have high interfacial energies of 9.7 mJ · m⁻² for PE/PA and 4.6 mJ · m⁻² for PE/PC and that the method of calculation does not influence the results. The interfacial energy between PE and nanotubes is in the range of 27 mJ · m⁻² which is very high. In contrast, the interfacial energy between the nanotubes and the matrix polymers is much lower. Here, the method of calculation matters and leads to

lower values when using the harmonic-mean equation. For example, at 240 °C the interfacial energy between MWNT and PE is 27.2 mJ · m⁻² whereas the interfacial energy between PA and MWNT is only 4.5 mJ · m⁻² (geometric-mean equation).

When calculating the wetting coefficients by setting polymer A as PE the results (Table 3) show negative values lower than –1 for both systems, illustrating that there is an interfacial energy driven localization of the nanotubes in the matrix polymers PC and PA.

Values of the wetting coefficients below –1 were also calculated when using the interfacial energy values of MWNT as given in ref.^[20] where the MWNT showed a somehow lower polarity of 37%.

The effect of a limited migration of nanotubes from a pre-filled phase into another phase within a blend was already reported in literature. Wu and Shaw^[21] reported some extent of nanotube transfer from a (highly) pre-filled PE-terephthalate masterbatch towards a second polymer component during injection moulding of dry mixed 50/50 vol.-% mixtures. In case of PE and PP, where the approach of the wetting coefficient according to their

Table 2. Interfacial energies as calculated using harmonic and geometric mean equations.

Materials	Temperature	Interfacial energy acc. to harmonic mean equation	Interfacial energy acc. to geometric mean equation
	°C	mJ · m ⁻²	mJ · m ⁻²
PE/PA	240	9.7	9.7
PE/PC	280	4.6	4.6
PE/MWNT	240	27.4	27.2
PA/MWNT	240	8.5	4.5
PE/MWNT	280	27.1	27.0
PC/MWNT	280	15.6	9.4

Table 3. Wetting coefficients as calculated using interfacial energies as obtained by harmonic and geometric mean equations.

System A/B/ CNT	Temperature	Wetting coefficient ω_A acc. to harmonic mean equation	Wetting coefficient ω_a acc. to geometric mean equation
	°C	$\text{mJ} \cdot \text{m}^{-2}$	$\text{mJ} \cdot \text{m}^{-2}$
PE/PA/CNT	240	-1.95	-2.32
PE/PC/CNT	280	-2.50	-3.83

calculations indicated nanotube location at the interface, the counted area fraction of migrated nanotubes was 7%, whereas for polyvinylidene fluoride and PA6,6 the prediction indicated nanotube location in PET. However, no polymer pair was involved for which nanotube location in the formerly unfilled phase was predicted and, thus, the migration effect as described above for PE-MWNT concentrates could not be studied.

Conclusion

The presented new way of introducing nanofillers in a polymer matrix uses the effect of filler migration due to different interfacial energies between the filler and the base polymer of the concentrate and the diluting polymer. The phenomenon of nanofiller migration was especially observed in literature for layered silicates^[22–24] but also in some extent for nanotubes^[21] and is in most cases undesired. Here, this effects is thermodynamically driven and can be used to disperse the nanofiller in the matrix. Since the nanofiller was homogeneously dispersed in the concentrate due to the special way of the concentrate synthesis, this dispersion could be transferred into the matrix polymers. This method seems to be very effective in order to get nicely dispersed nanocomposites. The effect is strongly connected to the better compatibility of nanotubes with the matrix materials than with the coating PE. Therefore, we expect that the concept may be extended to other polymer matrices which show a polar character and high immiscibility with PE. The improved dispersion of the nanotubes leads to significant lower electrical percolation thresholds of these nanocomposites as compared to direct incorporation of the same kind of nanotubes under the same mixing conditions. In this context, the concentrate with the lowest MWNT content (24 wt.-%) resulted in the lowest electrical percolation threshold, whereas the concentrate with the highest loading (44 wt.-%) led to the lowest resistivity values.

However, the nanocomposite prepared by this strategy represents a blend structure with the amount of the carrier component PE coupled to the nanotube content. Even if we

may assume that such small contents of a second blend component do not play an important role, the effects on other properties, like mechanical behaviour, have to be studied in future investigations. In addition, the kinetics of nanofiller migration has to be investigated in more detail, since the mixing time used in this study in a small scale compounder was relatively high.

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- [1] J. N. Coleman, U. Khan, Y. K. Gun'ko, *Adv. Mater.* **2006**, *18*, 689.
- [2] E. T. Thostenson, Z. Ren, T.-W. Chou, *Compos. Sci. Technol.* **2001**, *61*, 1899.
- [3] O. Breuer, U. Sundararaj, *Polym. Compos.* **2004**, *25*, 630.
- [4] S. C. Tjong, *Mater. Sci. Eng., R* **2006**, *53*, 73.
- [5] J.-H. Du, J. Bai, H.-M. Cheng, *eXPRESS Polym. Lett.* **2007**, *1*, 253.
- [6] L. Bokobza, *Polymer* **2007**, *48*, 4907.
- [7] M. Moniruzzaman, K. I. Winey, *Macromolecules* **2006**, *39*, 5194.
- [8] R. Andrews, D. Jacques, M. Minot, T. Rantell, *Macromol. Mater. Eng.* **2002**, *287*, 395.
- [9] D. Bonduel, M. Mainil, M. Alexandre, F. Monteverde, P. Dubois, *Chem. Commun.* **2005**, 781.
- [10] P. Dubois, M. Alexandre, *Adv. Polym. Mater.* **2006**, *8*, 147.
- [11] S. Peeterbroeck, B. Lepoittevin, E. Pollet, S. Benali, C. Broekaert, M. Alexandre, D. Bonduel, P. Viville, R. Lazzaroni, P. Dubois, *Polym. Eng. Sci.* **2006**, *46*, 102.
- [12] WO 128261 (2006), International Application No.: PCT/BE2006/000061, invs.: M. Alexandre, D. Bonduel, M. Claes, P. Dubois, S. Peeterbroeck, S. Pegel, P. Pötschke.
- [13] K. Wiemann, W. Kaminsky, F. H. Gojny, K. Schulte, *Macromol. Chem. Phys.* **2005**, *206*, 1472.
- [14] W. Kaminsky, A. Funck, K. Wiemann, *Macromol. Symp.* **2006**, *239*, 1.
- [15] U. Sundararaj, C. W. Macosko, A. Nakayama, T. Inoue, *Polym. Eng. Sci.* **1995**, *35*, 100.
- [16] M. Sumita, K. Sakata, S. Asai, K. Miyasaka, H. Nakagawa, *Polym. Bull.* **1991**, *25*, 265.
- [17] S. Wu, "Polymer Interface and Adhesion", Marcel Dekker Inc., New York 1982.

- [18] <http://www.surface-tension.de/solid-surface-energy.htm>, accessed June 15th 2007.
- [19] S. Nuriel, L. Liu, A. H. Barber, H. D. Wagner, *Chem. Phys. Lett.* **2005**, *404*, 263.
- [20] H. Barber, S. R. Cohen, H. D. Wagner, *Phys. Rev. Lett.* **2004**, *92*, 186103.
- [21] M. Wu, L. Shaw, *J. Appl. Polym. Sci.* **2006**, *99*, 477.
- [22] S. S. Ray, S. Pouliot, M. Bousmina, L. A. Utracki, *Polymer* **2004**, *45*, 8403.
- [23] M. Gahleitner, B. Kretzschmar, G. van Vliet, J. Devaux, D. Pospiech, K. Bernreitner, E. Ongolic, *Rheol. Acta* **2006**, *45*, 322.
- [24] P. Pötschke, B. Kretzschmar, A. Janke, *Compos. Sci. Technol.* **2007**, *67*, 855.