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Mechanical properties and electrical conductivity of carbon-nanotube filled polyamide-6 and its blends with acrylonitrile/butadiene/styrene

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Abstract

Composites of polyamide-6 and carbon nanotubes (NT) have been prepared on a corotating twinscrew extruder. It is shown by transmission electron microscopy (TEM) that the nanotubes are dispersed homogeneously in the polyamide-matrix. The electrical conductivity of these composites was analyzed and compared to carbon black filled polyamide-6. It is found that the NT-filled polyamide-6 shows an onset of the electrical conductivity at low filler loadings (4–6 wt%). In agreement with rheological measurements this onset in the conductivity is attributed to a percolation of nanotubes in the insulating matrix polymer. Tensile tests of the NT-composites show a significant increase of 27% in the Young's modulus, however the elongation at break of these materials dramatically decreases due to an embrittlement of the polyamide-6. Blends of these composites and Acrylonitrile/butadiene/styrene (ABS) have been prepared by extrusion. It is shown by TEM measurements that the nanotubes are selectively located in the polyamide-6. These selectively filled polyamide-6/ABS-blends show a highly irregular, cocontinuous morphology. Due to the confinement of the conductive filler to one blend component these materials show an onset in the electrical conductivity at very low filler loadings (2–3 wt%). These findings are explained by a double percolation effect. The NT-filled blends show superior mechanical properties in the tensile tests and in IZOD notched impact tests.

Keywords: Carbon nanotubes; Polyamide/ABS-blend; Conductivity

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1. Introduction

In recent years, there has been intense interest in multiphase polymer blends due to the potential opportunities of combining the attractive features of each blend component while at the same time reducing their deficient characteristics [1,2]. However, binary blends of immiscible polymers generally exhibit poor mechanical properties due to a coarse and often unstable morphology, such as in polypropylene/polyamide blends [3]. Therefore it is essential to control and stabilize a desired type of morphology in a polymer blend in order to generate polymeric materials with favorable properties.

In the past it was shown that a cocontinuous morphology often accounts for a synergistic improvement of the blend properties [4–7]. The thermodynamically unstable cocontinuous morphology is often observed for blends of a composition near phase inversion. Such morphologies can be stabilized by the use of a compatibilizer, which resides at the polymer/polymer interface and reduces the interfacial tension between the blend components [8–10] and prevents coalescence via steric stabilization [11–14]. The compatibilizer can either be premade or formed in situ during melt processing (reactive compatibilization).

In the development of blends based on polyamides the concept of reactive compatibilization has been described extensively [15–24]. Especially blends of polyamide-6 and acrylonitrile/butadiene/styrene (ABS) are of significant commercial interest, due to their improved toughness particularly at low temperatures. ABS consists of butadiene rubber dispersed in a matrix of poly(styrene-*co*-acrylonitrile) (SAN). The preferred route to compatibilze these blends has been to add a polymer, which is capable of

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reacting with the amine-functionality of the polyamide and which is also miscible with the SAN phase of ABS. The use of terpolymers of styrene, acrylonitrile and maleic anhydride as effective compatibilizers for polyamide-6/ABS-blends is described extensively in patents [25–27].

Steinmann et al. have shown that a cocontinuous morphology can also be stabilized by selectively filling one phase of a binary blend [28]. PS/PMMA-blends in which the PMMA phase was selectively filled with nanoscale glass beads were characterized with respect to the stability and the broadness of the phase inversion region. It was found that the filler not only stabilizes the cocontinuous morphology observed at the phase inversion concentration but also broadens the phase inversion region, the concentration range in which cocontinuity can be observed.

A common characteristic of most polymeric materials is their high electrical resistivity, which accounts for the insulating character of these materials. While for many applications this feature is highly desirable, there are also numerous applications for which an electrically conducting behavior would be advantageous. The conventional method to enhance electrical conductivity of polymers is to compound the polymer with conductive carbonaceous fillers. In this case with increasing filler content the electrical conductivity increases by orders of magnitude at the percolation threshold, which depends on the dispersion state and geometry of the filler. In order to obtain materials with high conductivity, high loading of conductive filler is needed. This, however, not only increases the final cost of the material due to the high cost of the filler, but also often impairs the mechanical properties of the material.

Recently, increasing attention has been given to the incorporation of conductive fillers into immiscible polymer blends in order to improve the conductivity at much lower filler contents due to a double percolation phenomenon. Double percolation refers to the percolation of a filler within one phase of a polymer blend (first percolation), which itself percolates in the blend (second percolation). Sumita et al. have shown that for HDPE/iPP blends electrical conductivity can be observed at carbon black loadings of less than 1 phr [29]. In this case, the filler is located preferentially in the HDPE domains of the blend. The electrical conductivity is explained by a double percolation phenomenon. Within the HDPE domains the filler percolates which causes a conductivity of the HDPE domains. These domains percolate in the blend to form a continuous phase. In a second publication Sumita et al. have examined the conductivity of short carbon fiber filled HDPE/iPP blends [30]. In this case the percolation threshold of the filler should be considerably lower than in the case of spherical fillers due to the high aspect ratio of fibers. It was shown that the percolation threshold could be reduced considerably by selectively filling only the HDPE domains. However, in both publications Sumita et al. have not examined the effect of the filler on the mechanical properties of the blend.

Soares et al. have shown that the electrical conductivity of polystyrene–rubber blends loaded with carbon black which is localized at the interface is dramatically decreased [31]. Obviously, only a match of interaction energies of all blend components yields such a morphology. Their results allow to conclude that the type of carbon black and the locus of its action is decisive for improved conductivity.

Recently carbon nanotubes have been described as effective conducting fillers for polymers. Nanotubes can be described as long and slender fullerenes, in which the walls of the tubes are hexagonal carbon (graphite structure). These tubes can either be single walled (SWNT) or multi-walled (MWNT). In a recent review, Thorstenson et al. have described the use of nanotubes to produce composite materials with superior electric properties [32]. Moreover, carbon nanotubes are described to significantly improve the stiffness of polymers due to the high elastic modulus of nanotubes.

Only in a very recent paper by Pötschke et al. the influence of processing conditions on the state of dispersion of MWNT in polymeric matrices has been described [33]. It was shown that the nanotubes have been dispersed uniformly through the matrix by compounding a polycarbonate master batch with the corresponding neat polymer in a twin-screw compounder. No signs of segregation or depletion of MWNT at the surface of extruded samples was found.

From the findings stated above, one can presume a number of effects caused by the addition of carbon nanotubes to polyamide-6/ABS-blends. Firstly, the stability of the cocontinuous morphology should be improved by the addition of a reactive compatibilizer and the filler, if one manages to confine the filler to one phase of the blend. Secondly, in this case electrical conductivity should be observed at rather small loadings of nanotubes in the blend due to a double percolation phenomenon [34]. Thirdly, due to the high stiffness of nanotubes the mechanical properties should be influenced substantially.

It is the aim of this paper to investigate systematically the filler dispersion and morphology of carbon nanotube filled polyamide-6 and its blends with ABS with respect to the electrical and mechanical properties of these materials. The percolation of carbon nanotubes is described by measurements of the electrical conductivity and is compared to results derived from rheological experiments.

2. Experimental part

2.1. Materials

The polyamide-6 (PA-6) material used in this work is the commercially available Durethan B30 by Bayer AG ($M_n = 20,000$ g/mol). The ABS material (cABS) was also supplied by Bayer. It is a precompound which consists of a proprietary amount of polybutadiene grafted with poly-

Table 1
Carbon nanotubes and carbon black filled polyamide-6

Sample	Nanotubes (wt%)	Carbon black (wt%)	Young's modulus (MPa)	Resistivity (Ω cm)
PA6	–	–	2590	$>10^{10}$
PA-NT-2	2	–	2980	$>10^{10}$
PA-NT-3	3	–	3310	$>10^{10}$
PA-NT-4	4	–	3490	$>10^{10}$
PA-NT-5	5	–	3340	6.4×10^{8}
PA-NT-6	6	–	3760	1.4×10^{7}
PA-NT-8	8	–	3960	2.4×10^{4}
PA-NT-10	10	–	4130	1.7×10^{3}
PA-NT-12	12	–	4180	2.8×10^{1}
PA-CB-5	–	5	2990	$> 10^{10}$
PA-CB-10	–	10	3390	1.8×10^{5}
PA-CB-15	–	15	3670	7.3×10^{2}
PA-CB-20	–	20	3970	4.3×10^{1}

(styrene-*co*-acrylonitrile-*co*-butadiene) (ABS), poly(styrene-*co*-acrylonitrile) (SAN) and the compatibilizer to obtain an optimized cocontinuous morphology. The carbon nanotubes were supplied as a master batch RMB4020-00 (RMB) by Hyperion Catalysis International, Cambridge, MA. The nanotubes are vapor grown and typically consist of 8–15 graphitic layers wrapped around a hollow core with a diameter of approximately 5 nm. The nanotubes show a typical diameter of 10–15 nm. They are produced as agglomerates and exist as curved intertwined entanglements [35,36]. The content of nanotubes in the master batch was determined by the supplier to be 20.3 wt%. The carbon black used in this work was Printex XE-2B (CB) by Degussa–Hüls.

2.2. Compounding and specimen preparation

Neat polyamide-6 (PA-6) was extruded with the carbon nanotube master batch (RMB) using a corotating twinscrew extruder (Werner and Pfleiderer ZSK25) at a barrel temperature of 260 °C, a screw speed of 200 rpm and a throughput of 5 kg/h to produce the samples PA-NT-x (x being the weight percentage of nanotubes in the composite) and PA-CB-x (x being the weight percentage of carbon black in the composite) presented in Table 1. In a second extrusion step under the same conditions these materials were compounded with cABS resulting in the polyamide-6/ABS-blends PA-ABS-NT-x and PA-ABS-CB-x presented in Table 2. All of these blends show the same cABS-content. The dried pellets were injection-molded into test specimens according to DIN 53455 on a Ferromatic Milacron K40. The moulding temperature was 250–260 °C and the mold temperature was 70 °C.

2.3. Measurement of electrical conductivity

Injection molded test bars with the dimensions 5 cm × 0.2 cm × 0.6 mm were cryo-fractured into specimens with a thickness of approximately 2 mm. The fracture surface was covered with silver paste to ensure good contact of the sample surface with the electrodes. Gold wire was used as electrode material. The conductivity was measured in dry air at ambient temperature using a Zahner Elektrik IM5d potentiostat. The volume resistivity of polyamide-6 was measured according to DIN IEC60093.

2.4. Mechanical characterization

Tensile tests were conducted using a Zwick tensiometer (model Z005 (ISO/DP 527)). The notched impact strengths of the compounds were tested with pendulum impact tester by Zwick (model 5102 (ISO 180/1A)). All tests were conducted at room temperature with test specimens dry as molded.

2.5. Rheological measurements

Rheological measurements were carried out on a mechanical spectrometer UDS200 (Paar Physica), a stress-controlled rheometer with parallel plate geometry. Injection

Table 2
Carbon nanotubes and carbon black filled polyamide-6/ABS-blends

Sample	PA-6 content (wt%)	cABS content (wt%)	Nanotubes (wt%)	Carbon black (wt%)	Young's modulus (MPa)	Elong. at break (%)	Notched IZOD impact strength (kJ/m^2)	Resistivity (Ω cm)
PA-ABS-NT-0	45.0	55	–	–	1970	105 ± 15	71	$>10^{10}$
PA-ABS-NT-1	44.6	55	0.4	–	2040	80 ± 14	n/a	$>10^{10}$
PA-ABS-NT-2	44.1	55	0.9	–	2100	70 ± 12	60	$>10^{10}$
PA-ABS-NT-4	43.2	55	1.8	–	2150	65 ± 13	55	$>10^{10}$
PA-ABS-NT-5	42.8	55	2.2	–	2160	60 ± 15	56	2×10^{8}
PA-ABS-NT-6	42.3	55	2.7	–	2200	54 ± 9	53	1.5×10^{5}
PA-ABS-NT-8	41.4	55	3.6	–	2270	52 ± 11	n/a	9.1×10^{4}
PA-ABS-NT-10	40.5	55	4.5	–	2330	49 ± 13	n/a	6×10^{3}
PA-ABS-NT-12	39.6	55	5.4	–	2410	52 ± 9	44	1×10^{3}
PA-ABS-NT-16	37.8	55	7.2	–	2510	44 ± 11	28	1.7×10^{2}
PA-ABS-CB-5	42.8	55	–	2.2	1800	42 ± 9	54	$> 10^{10}$
PA-ABS-CB-10	40.5	55	–	4.5	1970	21 ± 7	17	1.2×10^{7}
PA-ABS-CB-15	38.3	55	–	6.7	2090	24 ± 1	11	6.8×10^{3}

molded samples were of disc shape with a diameter of 25 mm and a thickness of 1 mm. All measurements were conducted under nitrogen atmosphere to avoid oxidative degradation. The strain region, in which the material can be regarded linear viscoelastic was determined by amplitude sweep experiments and is in the order of 5%. Isothermal frequency sweeps were taken at 260 °C.

2.6. Transmission electron microscopy

The morphology of the samples was examined by transmission electron microscopy (TEM). For TEM measurements, ultra thin sections were prepared at −60 °C with an Ultracut E ultramicrotome by Reichert and Jung using a diamond knife. Measurements were carried out on a LEO 912 Omega (120 kV).

3. Results and discussion

3.1. Carbon-nanotube filled polyamide-6

3.1.1. Morphology and conductivity

The morphology of carbon nanotube filled polyamide-6 was investigated by TEM methods. Fig. 1 shows TEM micrographs of a composite containing 5 wt% carbon nanotubes. In Fig. 1a one can observe dark areas of the size of approximately 100 nm. These areas represent regions of relatively high concentrations of carbon nanotubes in the composite. Besides these clusters of nanotubes the filler is dispersed uniformly in the polymer matrix. At higher magnification (Fig. 1b) the individual nanotubes are recognizable as long hollow fibers with a diameter of 10–15 nm. A preferred orientation is not observed. Similar structures of carbon nanotubes in a polymer matrix have been observed by Qian et al. for NT-filled polystyrene [37]. The dispersion of the nanotubes as displayed in these TEM-micrographs suggests a formation of a nanotube network in a polyamide-6 matrix. Rheological evidence for this phenomenon will be given below.

The resistivity of the composites PA-NT-*x* was measured as described in Section 2 and is compared with values of the PA-CB-*x* samples. The results are shown in Fig. 2. The resistivity range in our experimental set-up is limited to values below 10^{10} Ω cm as shown in Fig. 2. Therefore in the case of the sample PA-CB-5 a range of the resistivity is proposed due to the inaccuracy of the measurement. In both the nanotube filled and the carbon black filled polymide-6 composites the resistivity levels off at approximately 10–100 Ω cm at high filler loadings. However the drop-off in the resistivity occurs at lower filler loadings in the case of the nanotube filled polyamide-6.

From the data available this drop off occurs in the range between 3 and 7 wt% nanotubes. In the case of the carbon black filled polyamide-6 a comment on the drop-off in the resistivity can not be made accurately due to the lack of experimental data in the filler range between 5 and 10 wt%, but the data available suggests that this drop-off occurs at higher filler loadings than in the case of the NT-filled polyamide-6. The difference between both samples can be explained on the basis of percolation theory by different percolation thresholds for both types of fillers [38]. When adding an electrically conducting filler to an insulating polymer matrix the resistivity of the composite drops by orders of magnitude when the percolation threshold is reached. The nanotubes show a high aspect ratio (100–1000), therefore in this case the percolation threshold should be reduced dramatically. As described by Garboczi et al. the intrinsic conductivity of a conducting filler in an insulating matrix can be defined in analogy to the intrinsic viscosity as:

$$[\sigma] = \lim_{\phi \to 0} \sigma_{\mathrm{red}}$$

with σ_{red} being the reduced conductivity:

$$\sigma_{\mathrm{red}} = \frac{\sigma_{\mathrm{eff}} - \sigma_{\mathrm{m}}}{\sigma_{\mathrm{m}}\phi}$$

In this equation, σ_{eff} is the conductivity (the reciprocal of the resistivity) of the composite and σ_{m} the conductivity of the matrix. In Fig. 3 the reduced conductivity of the nanotube filled samples is plotted versus the volume fraction of the filler. The intrinsic conductivity $[\sigma]$ has been determined by a linear extrapolation of the reduced conductivity to a volume content of $\phi_{\mathrm{NT}} = 0$. In this case, $[\sigma] \approx 2360$.

In the case of prolate fillers with high aspect ratio and a difference in conductivity between the matrix and the filler of orders of magnitude (superconducting filler), the intrinsic conductivity is given according to Garboczi et al.:

$$[\sigma] = \frac{(L/d)^2}{\ln(L/d)}$$

with L being the length of the prolate filler and d its diameter.

In our case, the experimentally determined value for $[\sigma] \approx 2360$ corresponds to an aspect ratio $(L/d) = 105$. This value is in accordance with values described in literature [39].

3.1.2. Rheology

Rheological experiments are another sensitive tool to investigate the percolation of a filler in a viscoelastic fluid. Therefore, we have conducted frequency sweeps at extrusion temperature (260 °C) of the PA-NT-*x* composites. In Fig. 4 the phase angle δ is plotted versus the absolute value of the complex modulus ($|G^*|$). In literature this plot is known as the van Gurp Palmen plot [40,41]. For the matrix polyamide-6 the curve approaches a phase angle of 90° at low complex moduli indicating the flow behavior of a viscous fluid. In contrast, the PA-NT-*x* samples with high nanotube contents resemble the behavior of an elastic solid with a corresponding equilibrium modulus, which can be

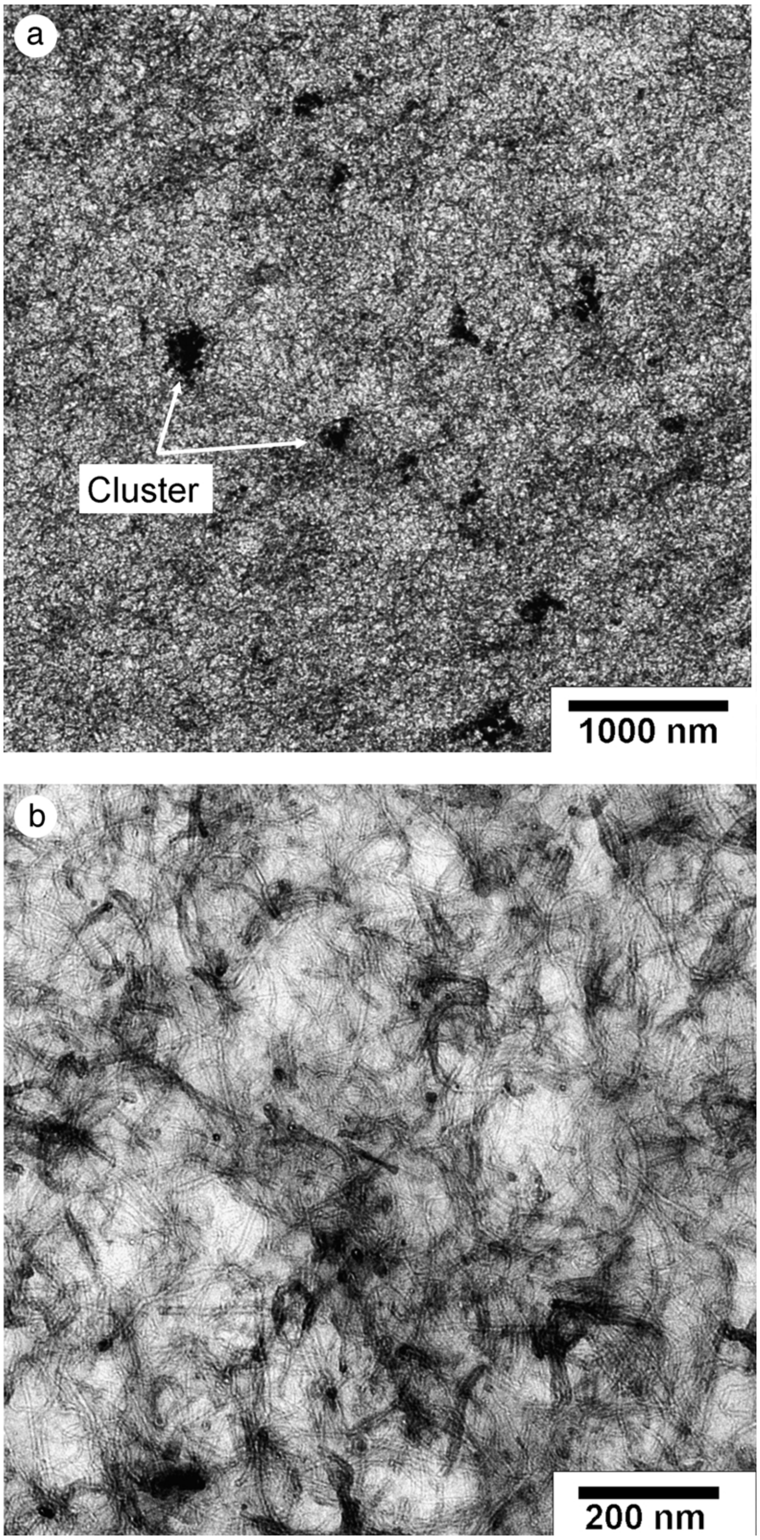

Fig. 1. TEM-micrographs of polyamide-6 filled with 5 wt% carbon nanotubes (PA-NT-5, a: 1000 nm scale bar, b: 200 nm scale bar).

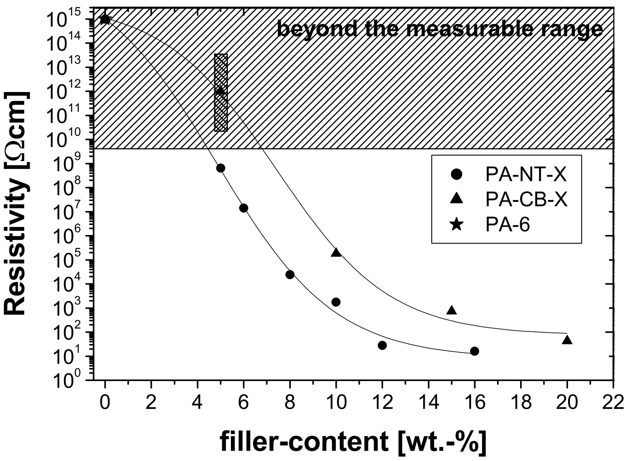

Fig. 2. Resistivity of polyamide-6 filled with nanotubes (●) or carbon blackc (▲) plotted versus the filler content.

determined by extrapolating the curves to a phase angle of $\delta = 0°$.

The phenomenon of a percolating filler in a viscoelastic fluid is rheologically equivalent to a fluid–solid transition. Gelation as an example for such a fluid–solid transition is extensively described by Winter et al. [42]. A well established method for the characterization of the gel-point is to plot the loss tangent (tan(δ)) versus the angular frequency (ω). At the gel point, tan δ is frequency independent. In the van Gurp plot this corresponds to a plateau at low complex moduli. From Fig. 4 we can estimate the filler concentration at which a gel-like behavior is observed. It is in the range between 2 and 4 wt%. Above this concentration the rheological behavior changes from a viscous fluid to an elastic solid indicating the build up of infinite clusters of nanotubes, i.e. the percolation threshold. According to theoretical studies, the percolation threshold for solid rods with an aspect ratio of 100 amounts to approximately 0.7 vol% [38]. In our case assuming a density of the nanotubes of $\rho^{NT} = 1.75\ \mathrm{g/cm^3}$ and that of polyamide-6 of $\rho^{PA} = 1.14\ \mathrm{g/cm^3}$ this percolation threshold corresponds to 1.1 wt%. The experimentally determined percolation threshold, as stated above, lies between 2 and 4 wt%. We explain the discrepancy between theory and experiment with two experimental findings. First, despite the fine dispersion of carbon nanotubes in the polymer matrix TEM-experiments (Fig. 1a) still show larger clusters of nanotubes. Secondly, the nanotubes, as shown in the TEM-micrographs cannot be assumed to be solid rods, but must be described as flexible and intertwined fibers. Both of these effects shift the percolation threshold to higher filler contents.

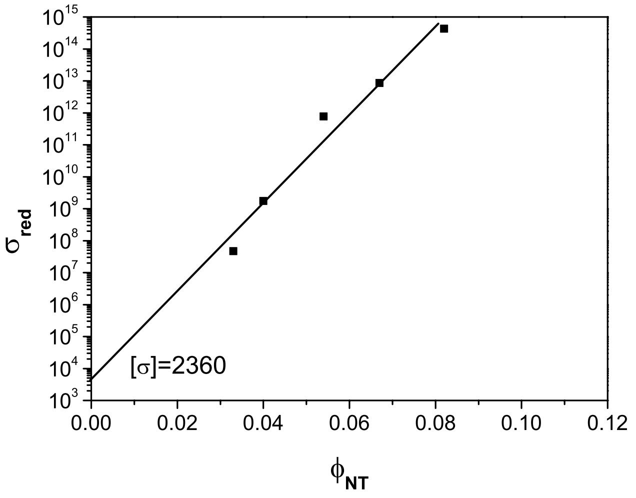

Fig. 3. The reduced conductivity of samples PA-NT-x plotted versus the volume content of the filler. The intrinsic conductivity is determined by the linear extrapolation to a volume content of $\phi_{NT} = 0$.

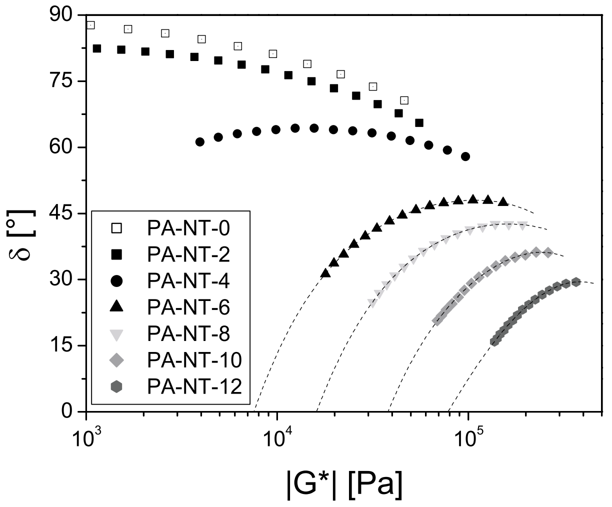

Fig. 4. Van Gurp plot of the PA-NT-x composites.

By extrapolating the van Gurp Palmen plots of the PA-NT-x composites for which a solid like behavior is observed (6–12 wt%) to a phase angle of $\delta = 0°$ we have determined the equilibrium moduli G_e of these samples. In Fig. 5 the G_e-values are plotted versus the filler content. A linear relation between the log of the equilibrium modulus and the filler content is found in the semi-logarithmic plot.

Due to their high elastic modulus, carbon nanotubes increase the stiffness in composite materials, as describe by Thorstenson [32]. Therefore, we have investigated the tensile properties of the PA-NT-x composites. In Fig. 6a the Young's modulus is plotted versus the filler content for the PA-NT-x and PA-CB-x composites. Fig. 6b shows the elongation at break of these materials.

All investigated samples show an increased modulus with increasing filler content. The PA-NT-composites are of significantly higher stiffness compared to the PA-CB-composites. Ideally, if the reinforcing filler (here the nanotube) bonded strongly to the matrix—what is obviously not the case here—the modulus of the composite would be even higher. Calculations based on a model used by Qian et al. would predict an modulus of about 7.6 GPa (we measured 3.7 GPa) for a compound containing 6 wt% of nanotubes with a aspect ratio of about 100 as determined from the conductivity measurements [37].

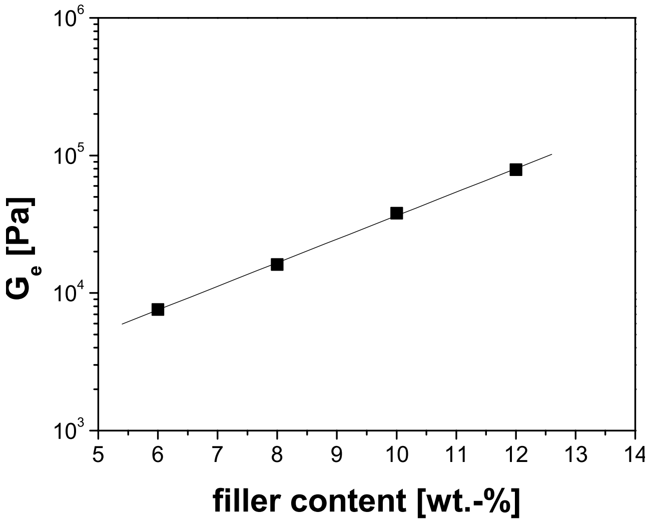

Fig. 5. Equilibrium moduli of the PA-NT-*x* composites plotted versus the filler content.

The elongation at break, as an indicator for the toughness of the materials, decreases dramatically when adding carbon nanotubes or carbon black to polyamide-6 (Fig. 6b). In both cases the material becomes brittle already at low filler contents.

We summarize that the carbon nanotubes used in this work show a percolation behavior in a polyamide-6 matrix at a filler content of 2–4 wt% nanotubes in both conductivity and rheological experiments. At the percolation threshold the volume–resistivity of PA-NT-*x* drops by orders of magnitude. The stiffness of these composites rises significantly with increasing filler content, however, the material becomes brittle already at low filler contents.

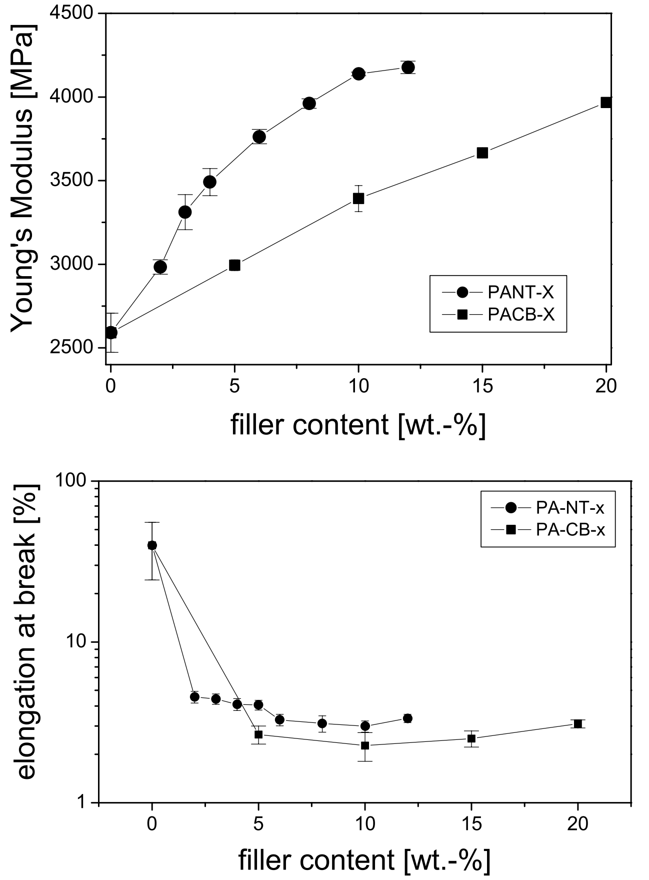

Fig. 6. Young's moduli (a) and elongation at break (b) of PA-NT-composites and PA-CB-composites plotted versus the filler content.

Now we investigate the morphological, electrical and mechanical properties of polyamide-6/ABS-blends in which the polyamide-6 phase is selectively filled with carbon nanotubes.

3.1.3. Carbon nanotube filled polyamide-6/ABS-blends

The morphology of carbon nanotube filled polyamide-6/ABS-blends was investigated by TEM methods. Fig. 7 shows TEM micrographs of the sample PA-ABS-NT-5. As shown for the PA-NT-*x* composites (Fig. 1) the carbon nanotubes are recognizable as long and narrow fibers in Fig. 7B. However unlike the PA-NT-*x* composites the nanotubes are not distributed homogeneously in the blend as can be seen in the overview Fig. 7B, in which two phases can be distinguished: a carbon nanotube rich phase, which represents the polyamide-6 and a phase with the spherical polybutadiene-particles of the size of approximately 200 nm, which represents the ABS-phase. No nanotubes are dispersed in the ABS-phase. Moreover from Fig. 7A, a highly irregular phase-structure of the polyamide-6 domains and the ABS-domains is observable, which we ascribe to a percolation of the polyamide-6 and the ABS domains resulting in a cocontinuous morphology.

As shown by Sumita et al. and Soares at al., a percolating electrically conducting phase in a binary polymer blend result in a material, which becomes electrically conducting at lower filler contents compared to the filled homopolymer due to a double percolation effect [29,30,31]. We have characterized the volume resistivity of the PA-ABS-NT-*x* composites. In Fig. 8 the resistivity of these samples is plotted versus the absolute filler content and is compared to the PA-NT-*x* composites. In both cases a decrease by orders of magnitude in the resistivity is observed. However in the case of the PA-ABS-NT-*x* series this decrease is observed at much lower filler contents. In agreement with the results by Sumita et al. we attribute this effect to the confinement of the electrically conducting filler to a percolating phase of polyamide-6 in the blend. Although the observed reduction in conductivity is remarkable, Soares et al. report in case of carbon black as filler about an even stronger reduction in conductivity, if the filler is in the interphase between both blend components. For given blend components such a behavior can be only observed if the surface energy of the filler matches values of the corresponding phases due to chemical treatment.

To investigate the effect of the nanotubes as a selective filler for the polyamide-6 phase on the mechanical properties of the blend we have conducted tensile tests and IZOD impact tests. Fig. 9 shows the Young's modulus and the

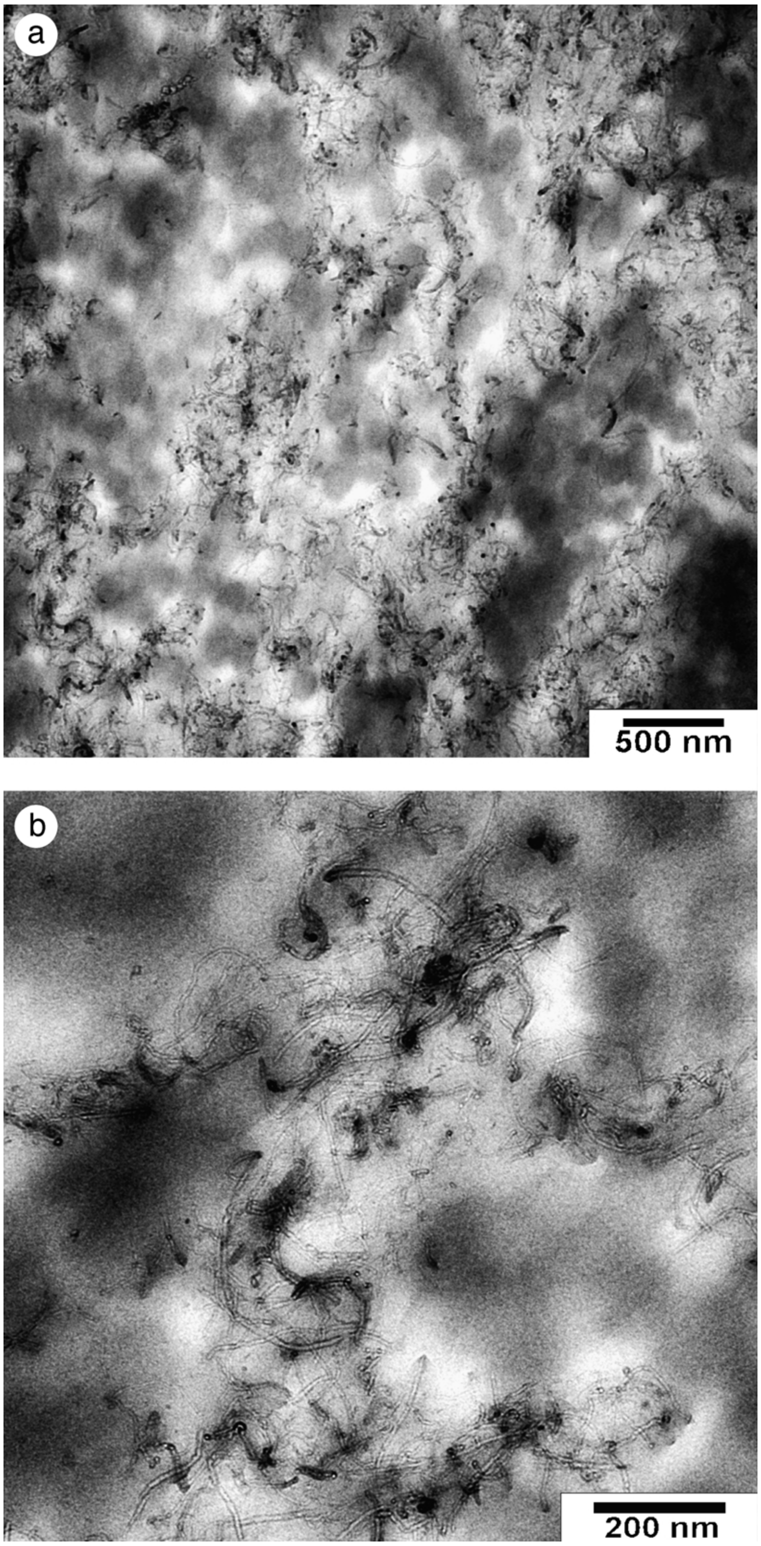

Fig. 7. TEM-micrographs of the PA-ABS-NT-5 composite (a: 500 nm scale bar, b: 200 nm scale bar). The carbon nanotubes are selectively located in the polyamide-6 phase.

elongation at break of these samples in dependence on the filler content. A comparison is made with polyamide-6/ABS-blends filled with carbon black.

The PA-ABS-NT-*x* composites show an increase in the Young's modulus with increasing filler content as shown in Fig. 9a. This increase is linear in the observed composition range. The unfilled blend shows a Young's modulus of 1970 MPa, while the blend with the highest loading of

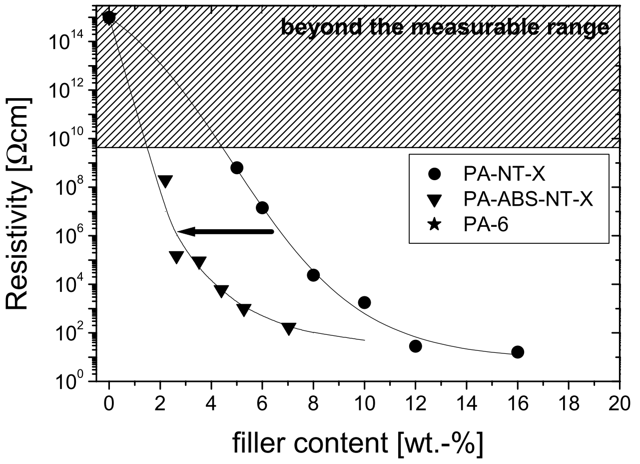

Fig. 8. Resistivity of PA-NT-*x* and PA-ABS-NT-*x* plotted versus the absolute filler content. The PA-ABS-NT-*x* composites show a decrease in the resistivity at lower filler loadings compared to the PA-NT-*x* composites.

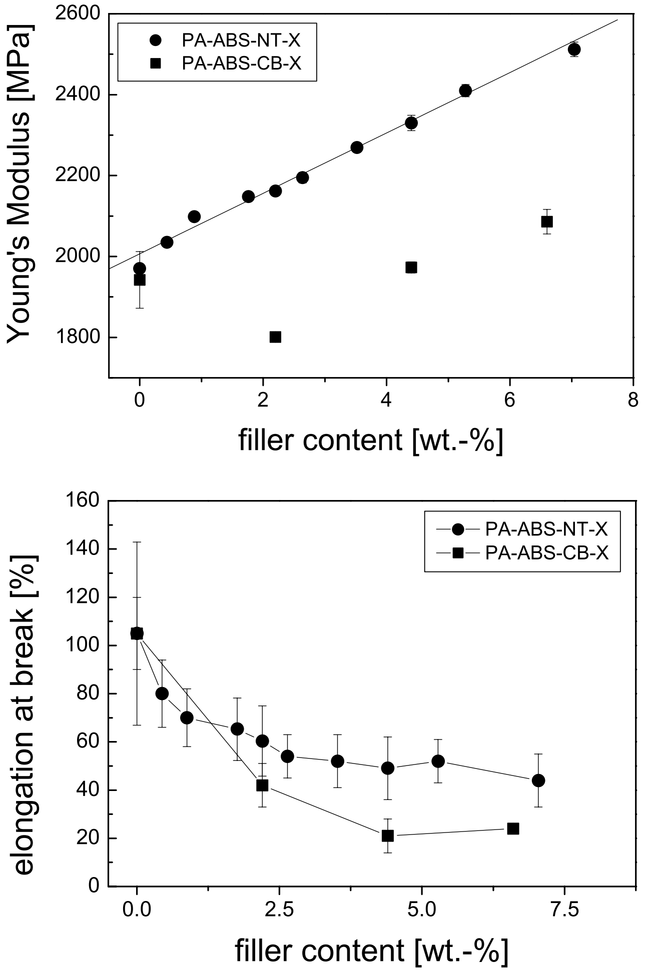

Fig. 9. Young's modulus (a) and elongation at break (b) of the PA-ABS-NT-*x* samples.

nanotubes (7 wt%) shows a modulus of 2510 MPa. This corresponds to an increase of 27%. In case of the carbon black filled blends a slight increase in stiffness is also observable in the high filler content region. This increase, however is much lower than in the case of the nanotube filled blends.

The elongation at break (Fig. 9b) of all investigated blends shows a different behavior in comparison to the filled polyamide-6 samples in the way that these samples show a yielding behavior in the entire filler loading range, while polyamide-6 shows a brittle behavior even at low filler contents. However, the elongation at break decreases with increasing filler content in both the NT-filled and the CB-filled blends. This decrease however is less pronounced in case of the NT-filled blends indicating a higher toughness of the NT-filled system.

To investigate the impact strength of the blends we have conducted notched IZOD impact tests. The results are plotted in Fig. 10.

The unfilled blend shows a notched impact strength of approximately 70 kJ/m^2. This value is indicative for a high toughness. With increasing filler content the notched impact strength decreases in both the NT-filled and the CB-filled blends. Up to a filler loading of approximately 2 wt% the decrease in the notched impact strength is comparable between the two series. At higher filler loadings the values of the PA-ABS-NT-*x* series are significantly higher than in the case of the CB-filled system. Thus these blends show a significantly higher toughness.

4. Conclusion

The electrical conductivity and the rheological properties of polyamide-6 filled with carbon nanotubes have been investigated systematically. Measurements of the electrical conductivity of nanotube filled polyamide-6 as well as rheological experiments suggest that nanotubes, a high aspect ratio nanoscale filler, show a percolation threshold of approximately 2–4 wt%. At percolation concentration the electrical resistivity of the composite drops by orders of

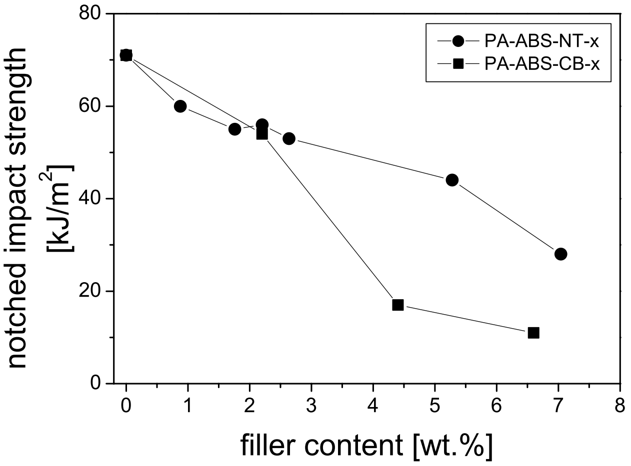

Fig. 10. IZOD notched impact strengths of the samples PA-ABS-NT-*x* and PA-ABS-CB-*x*.

magnitude and the material shows a fluid–solid transition in the molten state in rheological experiments. The mechanical properties of these composites were investigated and compared to carbon black filled polyamide-6. It was shown that the nanotubes cause a significant increase in stiffness, but, on the other hand, this material shows a brittle behavior indicated by the low elongation at break in the tensile test.

It could be shown that polyamide-6/ABS-blends of a composition of 55 wt% cABS and 45 wt% PANT-composites show a highly irregular morphology in which only the polyamide-6 phase is filled with nanotubes. These blends show electrical conductivity at significantly lower filler loadings compared to the filled homopolymer. This is explained by a double percolation effect. The nanotubes percolate in the polyamiode-6 phase (first percolation), which itself percolates in the blend (second percolation). These blends show increased stiffness. The notched impact strength of these materials decreases with increasing filler content, but the blends show a significantly higher toughness than blends filled with carbon black.

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