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# Percolation behavior and mechanical properties of polycarbonate composites filled with carbon black/carbon nanotube systems

**Summary** — The effect of a mixed filler system consisting of carbon black (CB) and multi-walled carbon nanotubes (MWCNTs) on electrical, rheological and mechanical properties of melt compounded composites with polycarbonate (PC) was investigated. Pure CB or MWCNTs or mixtures of CB and MWCNTs in mass ratio 50/50 or 75/25 were added to PC using a small scale DACA Micro-Compounder in order to get the filler concentration between 0.5 and 5 wt. %. Comparison of the theoretical percolation concentration for composites with the mixed filler systems with corresponding experimental values allows to state that no synergistic effect occurs. SEM and TEM investigations on thin sections showed a good distribution of quite small CB aggregates and good dispersion of the MWCNTs in composites. Rheological properties of the melted composites are more influenced by MWCNTs than by CB content. The stress-strain behavior of the composites compared at loadings leading to a composite conductivity of $10^{-4}$ S/cm is the best for composites filled with MWCNTs and better for that with mixed filler systems than for composites with CB only.

**Keywords**: carbon nanotubes, polycarbonate, nanocomposite, dispersion, electrical conductivity, melt rheological properties, stress-strain behavior.

PERKOLACJA I WŁAŚCIWOŚCI MECHANICZNE KOMPOZYTÓW POLIWĘGLANU NAPEŁNIANYCH MIESZANINAMI SADZA/NANORURKI WĘGLOWE

**Streszczenie** — Badano wpływ mieszanego układu napełniaczy złożonego z sadzy (CB) i wielościennych nanorurek węglowych (MWCNT) na elektryczne, reologiczne i mechaniczne właściwości kompozytów z poliwęglanem (PC). Czyste CB lub MWCNT albo mieszanki CB i MWCNT o stosunku masowym 50/50 lub 75/25 były dodawane do PC w ilości od 0,5 do 5 % mas. Zależności przewodności właściwej przygotowanych kompozytów od zawartości napełniacza opisywano funkcjami, których parametr dobieralny odpowiadał wartościom elektrycznego progu perkolacji ($p_c$). Porównanie tak wyznaczonych teoretycznych stężeń perkolacji kompozytów zawierających różne układy napełniaczy z odpowiednimi wartościami doświadczalnymi pozwoliło stwierdzić, że nie występuje tu żaden efekt synergiczny. Badania SEM i TEM cienkich przekrojów kompozytów wykazały dobrą dyspersję stosunkowo małych agregatów CB i dobry rozkład MWCNT w kompozytach. Właściwości reologiczne stopionych kompozytów są bardziej zależne od zawartości MWCNT niż od zawartości CB jako napełniacza. Charakterystyka naprężenie–odkształcenie jest najlepsza w przypadku kompozytów napełnionych MWCNT, nieco słabsza w przypadku kompozytów z mieszanym układem napełniaczy, a najsłabsza gdy kompozyt napełniono samym CB.

**Słowa kluczowe**: nanorurki węglowe, poliwęglan, nanokompozyt, dyspersja, przewodność elektryczna, właściwości reologiczne stopu, charakterystyka naprężenie-odkształcenie.

Electrically insulating properties of most of the polymeric materials are well known. However, for some applications electrostatic dissipative or conductive behavior is required like in antistatic housing applications, wire and cable sheathing, and shielding against electromagnetic interference.

Intrinsically conductive polymers, like polypyrrole or polyaniline, are very expensive and their processability is poor. Therefore the use of conductive fillers incorporated into the polymer is a quite common way to increase the electrical conductivity of the resulting composites. The properties of these composites are varied mainly as a function of the filler content. When the filler content reaches a critical value (so-called percolation threshold

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[1]), a sharp transition from the insulating to the conducting behavior of composites occurs with only a slight increase in electrical conductivity at further increase in filler content.

Carbon black (CB) has been used since decades as a convenient and cheap additive for thermoplastics and rubbers in electrically conductive applications. However, the contents necessary to get conductive pathways through the insulating matrices is much higher as compared to conductive fibrous fillers. These high filler contents (around 10 wt. % [2]) can lead to reduction in other material properties like processability, gloss, and mechanical properties.

A new class of conductive fillers are carbon nanotubes (CNTs) which were described as very effective fillers in polymeric matrices in order to get conductive materials at very low loadings [3]. This is due to the excellent electrical properties combined with the very high aspect ratio [as high as 1000 for multi-walled carbon nanotubes (MWCNTs)] which enables percolation of the fillers at much lower concentrations as compared to CB. During the last years CNTs were shown as excellent nanofillers for polymeric composites not only to get electrically conductive or antistatic polymers but also to produce composites with enhanced mechanical [4—10] or other properties. However, the price of CNT materials is still too high for many industrial applications.

Therefore, the use of hybrid filler systems that combine outstanding properties of CNTs with lower costs of other conductive fillers are of economic interest. In such composites synergistic effects are desired, meaning that the effect originating from the use of the hybrid filler system is larger than the summarized effects of individual fillers. As far as the electrical percolation threshold of mixed carbon filler systems is concerned, an equation developed by Sun *et al.* [11] based on the percolation threshold of single fillers by adapting the excluded volume approach can be used to identify the synergy. Most of the studies reported in the literature on the use of hybrid filler systems were performed on epoxy resins [12—17] and only small effects were found concerning the electrical percolation threshold when replacing parts of the nanotubes with other conductive fillers or when adding them [17]. However, it was found that the addition of CB increases the maximal achievable conductivity at higher loadings [17].

Hybrid filler systems have also been applied to rubber-based composites [18, 19]. Better CNTs dispersion, lower resistivity, and also a reduction in the percolation threshold were found when using CNTs and CB together in styrene-butadiene rubber. When looking at thermoplastics, only few results are reported about the use of two carbon fillers [11, 20—23]. In polyethylene, mixtures of carbon fibers and CB were described [21], where the fibers provide charge transport over large distances and CB particles improved interfiber contacts leading to a conductivity rise. A decrease in resistivity was observed when adding MWCNTs to CB filled PE-HD composites [22]. In a recent paper on polyamide 12 (PA 12) composites, mixed filler systems of CB and two different commercial MWCNTs were studied [23] and no synergistic effects concerning electrical percolation were found applying the model of Sun [11]. However, in mixed filler systems, similar to the findings in epoxy, at higher loadings also higher conductivity values were found than in composites with CNTs only [23]. The effect of non-conducting fillers, like organoclay in polyamide 6-CB (PA 6-CB) composite was reported in [24]. A reduction of CB percolation threshold was observed in the presence of a certain amount of organoclay, which was attributed to a nanoplatelet induced enhanced self-assembly of the CB network.
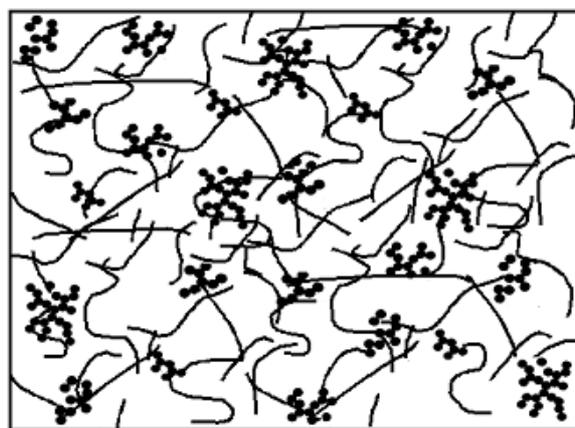


*Fig. 1. Scheme of a co-supporting network formed by MWCNTs and CB according to [23]*

The aim of this work was to use a mixed filler system consisting of MWCNTs and CB, thus combining a filler with a fiber like shape with a spherical shape filler. A combined network between both carbon nanofillers, as illustrated in Figure 1, was expected. Next the electrical properties, potential synergies in the percolation threshold, melt reological properties and the stress-strain behavior were investigated.

## EXPERIMENTAL

### Materials

As MWCNT material, a laboratory product from Nanocyl S.A. (thin straight and coiled nanotubes, crude material) with a mean tube diameter of 15 ± 5 nm with purity over 80 % was selected. CB of type Printex XE2 from Evonik Degussa GmbH, reportedly the best conductive industrially available CB, was chosen. According to the provider, Printex XE2 is characterized by specific surface area of 1000 m$^2$/g (determined using BET method), a carbon content of 99 % and represents an extra conductive gas CB with primary particles between 30 and 35 nm which form a highly aggregated structure.

Polycarbonate (PC) of type Iupilon E 2000 (Mitsubishi) in powder form was used as polymeric matrix.

All materials were dried before processing: polycarbonate at 120 °C for about 6 h and the carbon fillers at 100 °C for 2 h in vacuum.

**Preparation of samples**

MWCNT and CB were dry premixed using a mortar to obtain mass ratios of CB/MWCNT = 50/50 or 75/25 and were melt mixed with pure PC using a small scale DACA Micro-Compounder (DACA Instruments, Santa Barbara, USA, inner volume 4.5 cm$^3$) in order to get total filler concentrations in the range between 0.5 and 5 wt. %. Melt mixing was performed at 280 °C and 50 rpm for 15 min. The pure filler materials were treated in the same way. The sample input was 4.2 g. The obtained strands extruded using the set screw speed were compression molded at 260 °C and 50 kN to plates (60 mm in diameter, 0.5 mm thick) in order to perform electrical and mechanical testing.

**Methods of testing**

A Keithley electrometer Model 6517A equipped with an 8009 Resistivity Test Fixture was used to measure high resistivity samples using the full sample size of the pressed plates. Lower resistivity composites were measured by a four point test fixture combined with a Keithley electrometer Model 2000 using strips (20 mm × 3 mm) cut from the plates. All resistivity values were transformed into conductivity values. At least two measurements were performed for the sheets and eight for the strips.

Tensile tests were performed on small size dogbones cut from the pressed plates with a gauge 10 mm long. A universal testing machine Zwick Roell (2.5 kN) was used and the speed of 5 mm/min was applied. Seven samples were measured for each composition.

Melt rheological investigations were performed using an ARES oscillatory rheometer (Rheometric Scientific, USA) at 280 °C under nitrogen atmosphere. Frequency sweeps were carried out between 0.1 and 100 rad/s at strains within the linear viscoelastic range using parallel plate geometry (plates with diameter of 25 mm, gap of 1 to 2 mm). Scanning electron microscopy (SEM) was done on gold sputtered surfaces of samples cryofractured perpendicularly to the surface of the plates using LEO VP 435 microscope (Zeiss, Germany).

Transmission electron microscopy (TEM) of the two fillers and the composites was performed using an EFTEM LEO 912 (Leo, Germany) microscope at 120 KV equipped with an in-column OMEGA energy filter and a 2k slow scan CCD-camera (Proscan). For the composites, thin cuts 100 nm thick were prepared at room temperature from a middle position perpendicularly to the surface of the plates.

**RESULTS AND DISCUSSION**

The percolation threshold concentration ($p_c$) was investigated using DC volume conductivity measurements on pressed plates. The dependence of electrical volume
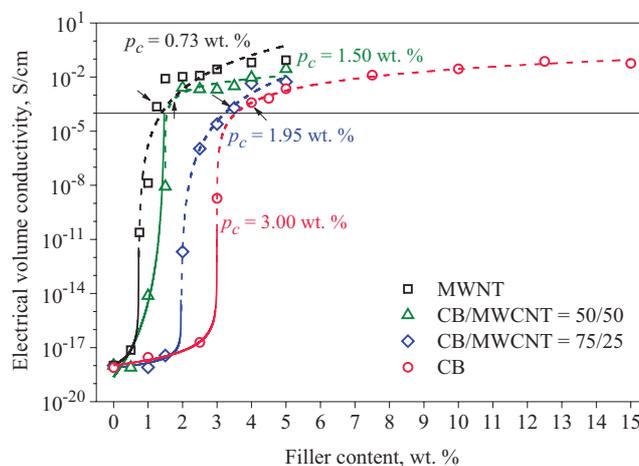


*Fig. 2. Effect of filler kind and content on electrical volume conductivity of prepared composites; the fitted values of percolation concentration ($p_c$) are given in the plot and the concentrations where a conductivity of $10^{-4}$ S/cm is reached are marked by arrows*

conductivity of prepared composites on the filler content is shown in Figure 2. Power law functions were used for curve fitting of the composite conductivity [σ(p)] for concentrations $p > p_c$ and $p < p_c$, respectively [1]:

$$\sigma(p) = B(p - p_c)^t \qquad (1)$$

and

$$\sigma(p) = B(p - p_c)^s \qquad (2)$$

where: *B — the proportionality constant, $p_c$ — the electrical percolation threshold, t, s — the critical exponents.*

The constants $B$, $p_c$, $t$ and $s$ were fitted using the method of mean squared error minimization. The fitted values of $p_c$ are included in Fig. 2. The lowest $p_c$ of 0.73 wt. % was found for samples with MWCNTs. Starting at 1.25 wt. % of MWCNTs the values of conductivity were higher than $10^{-4}$ S/cm representing the conductive range. The highest $p_c$ of 3 wt. % was observed for samples with CB and starting at 4 wt. % the conductivity values are in the conductive range. For samples with the mixed filler systems, $p_c$ values of 1.5 wt. % for CB/MWCNT = 50/50 and 1.95 wt. % CB/MWCNT = 75/25, which are between the values of the composites with pure fillers, were found.

The plots of conductivity versus the MWCNT content only, as done in Figure 3, show the effect of CB addition. It is clearly visible that the addition of CB to composites containing MWCNT reduces the MWCNT content needed for the electrical percolation. This is more apparent when the CB content in the filler mixture is higher. This is in contrast to the system of PA 12 with mixed
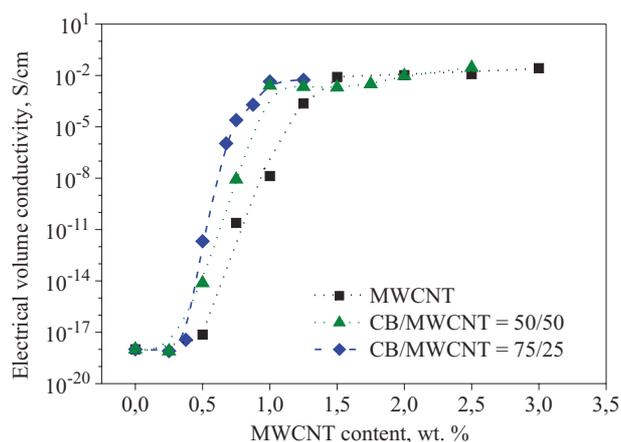
*Fig. 3. Electrical volume conductivity of prepared composites versus MWCNT content*

CB/MWCNT fillers reported in [23] where in the same kind of plot no differences were found between the use of pure MWCNTs and the MWCNTs with addition of CB. It can be assumed, that the formation of the conductive networks is dominated by the MWCNTs with their high aspect ratio. However, the additional conductive CB filler could lead to a better charge transport in the conductive pathways if localized mainly at the contact points between adjacent nanotubes or bridging nanotubes as it was presented in Figure 1. In order to check, if the reduction in $p_c$ (as it was shown in Figure 3) can be attributed to the synergistic effect, the model of Sun [11] was applied to our system:

$$\frac{m_{CNT}}{p_{c,CNT}} + \frac{m_{CB}}{p_{c,CB}} = 1 \qquad (3)$$
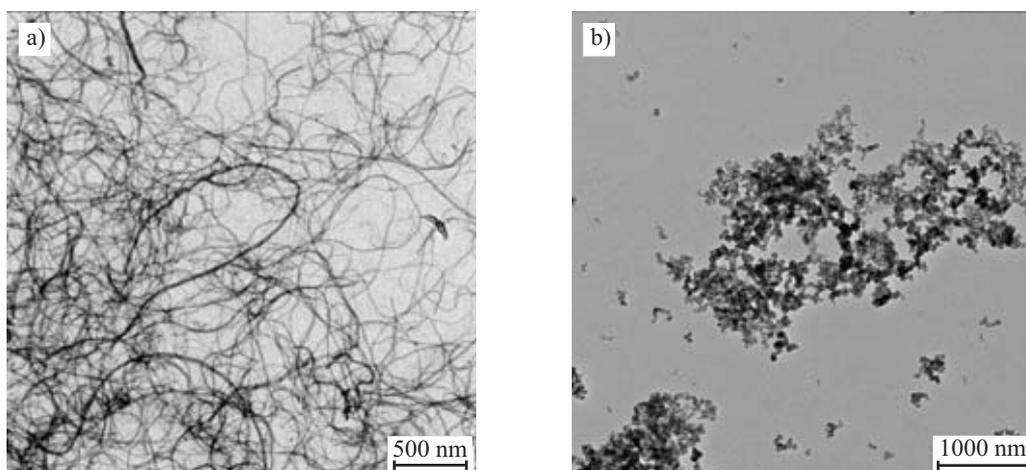


*Fig. 4. TEM images of: a) MWCNTs, b) CB*
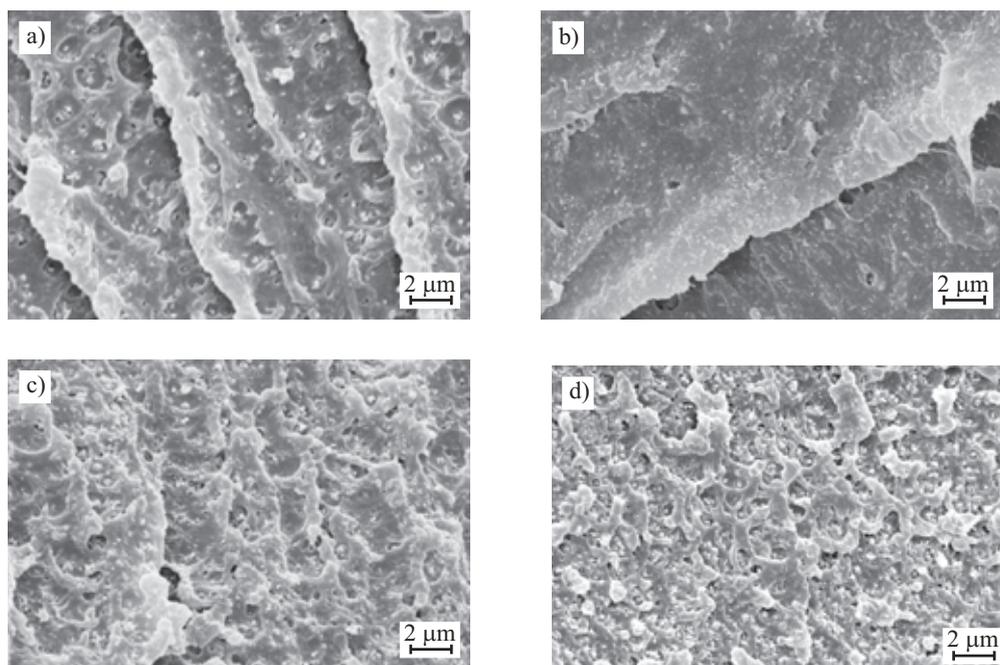


*Fig. 5. SEM of cryofractured samples (plates fractured perpendicularly to their surface) containing 2.5 wt. % of a) CB, b) MWCNT, c) CB/MWCNT = 50/50, d) CB/MWCNT = 75/25*
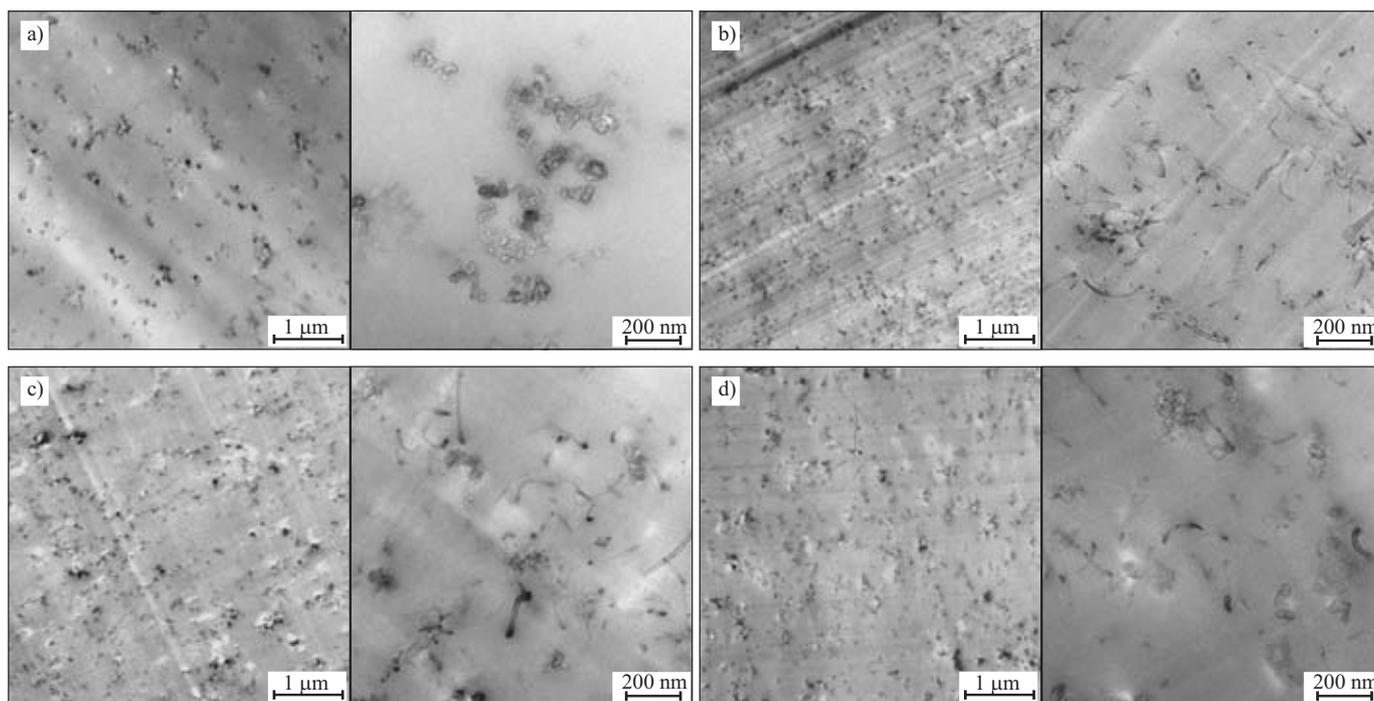
*Fig. 6. TEM images of thin sections of the composites (cut perpendicularly to the surface of the plates) containing 2.5 wt. % of: a) CB, b) MWCNT, c) CB/MWCNT = 50/50, d) CB/MWCNT = 75/25*

where: $m_{CNT}$, $m_{CB}$ — *the mass fractions of MWCNTs and CB, respectively*, $p_{c,CNT}$, $p_{c,CB}$ — *the corresponding percolation concentrations when MWCNT and CB are used alone.*

Synergism is only achieved if the measured $p_c$ for the mixed filler system is lower than that calculated from the measured values of the components. With $p_{c,CNT}$ as the corresponding electrical percolation threshold (here 0.73 wt. %) and $p_{c,CB}$ the electrical percolation threshold of CB (here 3 wt. %), the calculated percolation concentration for samples with mixed filler system CB/MWCNT = 50/50 was 1.17 wt. % of total filler content. In the experiment 1.5 wt. % of filler in PC was needed to achieve percolation. For the samples with filler CB/MWCNT = 75/25 the calculated theoretical percolation concentration was 1.67 wt. % of total filler content, however experimentally the value of 1.95 wt. % was found. The results indicate that no synergistic effect of the hybrid filler system can be found concerning the electrical percolation threshold for the investigated system. According to the interpretation of Sun [11] the results show that the conductive fillers disperse separately in the polymer matrix. Interestingly, all systems with higher filler content lead to the same conductivity value of about 0.1 S/cm, whereas in previous studies higher conductivity values were reported when using carbon based mixed filler systems [17, 23].

Morphological investigations were also performed. TEM images in Figure 4 illustrate the structure of MWCNT and CB fillers. The results obtained for the composite samples are shown in Figure 5 and 6. Composites with 2.5 wt. % of total filler content reveal good dispersion and distribution of both single fillers and the mixed filler systems. In the case of composites with pure CB filler a good distribution of quite small CB aggregates is seen. No big CB or MWCNT agglomerates can be observed what illustrates that the mixing process was adequate. However, even if TEM images of the composites with mixed filler systems reveal both nanofillers, no conclusions on the filler arrangement or the development of a common network between MWCNTs and CB can be drawn.

Melt rheological measurements of the different composite sets, as it is shown in Figure 7, reveal that the kind and content of filler influences complex melt viscosity ($\eta^*$). In all sets with different kind of filler a change from a liquid-like (Newtonian) behavior to a solid-like was visible at a certain filler concentration [25]. This transition occurs for samples with CB filler content between 2.5 and 3 wt. %, for samples with MWCNTs between 0.75 and 1 wt. %, for the samples with CB/MWCNT = 50/50 systems between 1.5 and 2 wt. %, and with CB/MWCNT = 75/25 below 1 wt. %. These findings are in relatively good correlation with the electrical percolation concentrations. Only for the system with CB/MWCNT = 75/25 filler the rheological percolation is observed at lower loadings than the electrical one. Figure 8 presents the complex viscosity of investigated systems at 0.1 rad/s versus the filler content. The graph clearly shows that increase in pure MWCNT content leads to the highest increase rate of $\eta^*$ value and CB content to the lowest rate. The composites with mixed filler systems are between those with pure fillers. From the composites characterized by constant volume conductivity of $10^{-4}$ S/cm, at frequency 0.1 rad/s, the system with CB (4 wt. %) shows a lower melt viscosity than the system with MWCNTs (1.25 wt. %). The compo-
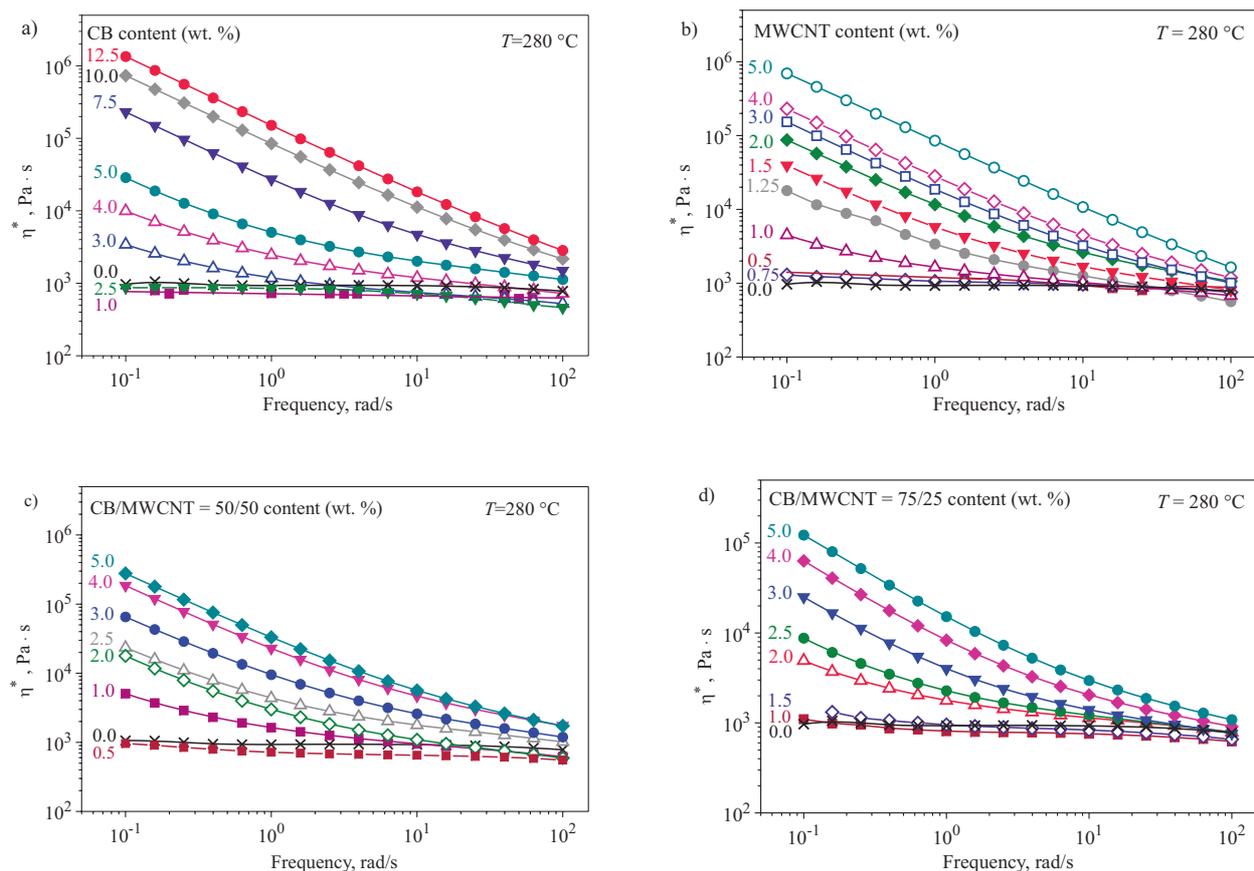
Fig. 7. Effect of frequency and filler content on complex viscosity ($\eta^*$) for systems of PC with different fillers: a) CB, b) MWCNT, c) CB/MWCNT = 50/50, d) CB/MWCNT = 75/25
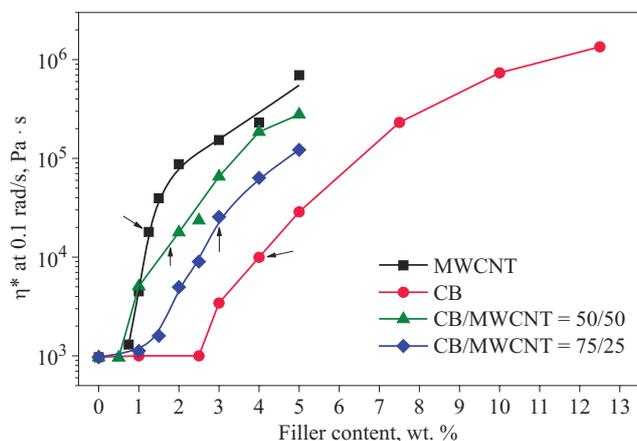


Fig. 8. Complex viscosity ($\eta^*$) at a measurement frequency of 0.1 rad/s versus filler content for PC with different fillers; the concentrations where conductivity of $10^{-4}$ S/cm is reached are marked with arrows



Fig. 9. Comparison of stress-strain curves of composites with various filler systems for which volume conductivity is about $10^{-4}$ S/cm which correspond to filler concentrations marked in Fig. 2 with arrows

site with CB/MWCNT = 50/50 (1.5 wt. %) follows a linear mixing rule, whereas the system with CB/MWCNT = 75/25 (3 wt. %) shows higher values than the pure fillers. This indicates that despite the different filler contents needed for percolation, the system with MWCNTs still leads to the highest viscosity values at the percolation threshold, which may be not favorable for processing.

However, at high frequencies, as usually applied in extrusion and injection molding, the differences in melt viscosity between different loadings and filler types diminish (compare Fig. 7 at 100 rad/s).

Mechanical testing was performed for all sets. As it is shown in Figure 9 the stress-strain-curves of pure PC produce a yield point at about 10 % strain and 55 MPa stress

followed by cold drawing with a strain hardening effect. As the stress at break is higher than the yield stress, for pure PC it represents the tensile strength at about 70 MPa. Elongation at break is at about 150 %. When the nanofillers content rises, an increase in modulus and stress at yield is observed and also the stress values above the yield point are enhanced. Starting at a certain nanofiller concentration, elongation at break decreases so that the break occurs also at lower stress values, in some case even below the yield stress. This concentration corresponding to decreased elongation at break is dependent on the fillers. Whereas for composites with CB filler high elongation at break occurs up to about 3 wt. % content, in samples filled with MWCNT this is observed only up to 1.25 wt. % content. The order of the concentrations at which significant reduction in elongation at break was observed, follows the percolation thresholds, even if the absolute values are not identical. In order to compare the samples, the concentrations at which an electrical volume conductivity of around $10^{-4}$ S/cm was achieved were selected and the stress-strain curves of these samples are plotted in Figure 9. This comparison of stress-strain curves at a constant composite conductivity clearly reveals the advantage of MWCNT over CB filler. 1.25 wt. % addition of MWCNT leads to higher yield stress and elongation at break than 3 wt. % addition of CB, whereas especially elongation at break is already reduced significantly. The system with 1.75 wt. % of mixed filler CB/MWCNT = 50/50 shows higher elongation at break but lower yield stress than the sample with 3 wt. % CB/MWCNT = 75/25. Obviously, the carbon nanotubes are favorable in keeping the mechanical property profile of PC, especially high deformability and the higher content of CB needed to get the same conductivity of the composite results in bigger brittleness. Also from the stress-strain behavior, no synergistic effects of the hybrid filler systems can be concluded.

## CONCLUSION

The polycarbonate composites with addition of CB, MWCNTs, or two mixtures of these fillers obtained by melt mixing show differences in electrical, rheological and mechanical behavior of the composites. In all mixtures a good dispersion and distribution of the carbon nanofillers could be observed with SEM and TEM methods. Composites with pure MWCNTs show lower electrical percolation, higher melt viscosity and a higher effect in the stress-strain behavior than those with pure CB and the mixed filler systems. As far as electrical percolation is concerned, using an equation of Sun [11], no synergistic effect between CB and MWCNTs could be found as the composites do not show lower percolation than calculated from the values of the pure fillers in PC.

On the other hand it was observed that the impact on melt viscosity of composites is larger when MWCNTs are used than for composites with CB. At a constant volume conductivity of $10^{-4}$ S/cm the viscosity (at 0.1 rad/s frequency) of the composite filled with 1.25 wt. % of MWCNT is nearly twice of that composite with 4 wt. % of CB. The evaluation of the stress-strain behavior of composites with a conductivity of $10^{-4}$ S/cm revealed values of elongation at break similar to those of pure insulating PC for the composite with pure MWCNTs and the composite with 1.75 wt. % of CB/MWCNT = 50/50 mixtures, whereas in the composite with pure CB there was found a significant reduction, down to about one-third of the value observed for the PC-MWCNT. The composite with 3 wt. % of CB/MWCNT = 75/25 showed values of elongation at break about two-thirds those measured for pure PC.

Interestingly, the filler combination of CB/MWCNT = 50/50 seems to have in summary a balanced property profile with improved mechanical properties as compared to pure CB, preserved high elongation at break as compared to PC and PC-MWCNT and only slightly reduced stress values as compared to PC-MWCNT. The melt viscosity of composites is lower than for the pure MWCNT filled system and only slightly higher than for composites with CB as filler. In addition, when looking from a price perspective, this mixed filler system may have an advantage. When a conductivity value of $10^{-4}$ S/cm is desired, the choice of composite with 0.875 wt. % of CB or with 0.875 wt. % of MWCNT may be cheaper in comparison to composite with 1.25 wt. % of MWCNT. As the ratio of the amount needed for percolation between MWCNTs and CB is about 1:4, based on that study economical advantages arise as long as the price ratio between MWCNTs and CB is larger than 4, which still is the current case. However, this study represents small-scale investigations on compression molded samples and has to be extended into industrial scale extrusion combined with injection molding in order to be applicable.

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