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STRUCTURE FORMATION SYNERGETICS AND PROPERTIES OF POLYPROPYLENE/CARBON NANOTUBE NANOCOMPOSITES

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Abstract. It has been shown that aggregation (tangled coils formation) of carbon nanotubes begins at their very small contents. This factor strongly reduces reinforcement degree of polymer/carbon nanotube nanocomposites. Estimation of the main parameters that influenced elasticity modulus of the mentioned nanocomposites was fulfilled. Theoretical calculations showed high potential of nanocomposites filled with nanotubes.

Keywords: nanocomposite, carbon nanotubes, aggregation, reinforcement degree, interfacial adhesion, synergetics.

1. Introduction

Recent studies [1, 2] allow to distinguish the carbon nanotubes (CNT) as the promising objects allowing to create materials with fundamentally new properties. CNT discovered in the 90s of the last century possess unique characteristics: great strength in combination with high elastic strain qualities, good conductivity and adsorbability properties, ability to electrons cold emission and gases accumulation, chemical and thermal stability, and so on.

There is a large number of CNT modifications, differing in layers number, sizes, network structure form and, hence, in properties. High cost of one-layered nanotubes (which makes up several dozens and even hundreds of US dollars per gram) requires selection of the nanomaterials which together with inherent high quality characteristics are accessible to industrial producers of nanocomposites, both with regard to production amounts as well as from the product realization perspective.

As it was shown earlier [3], polymer nanocomposites filled with CNT have a number of specific features. Therefore the purpose of the present paper is the study of the structure and reinforcement degree of polypropylene/CNT (PP/CNT) nanocomposites [4] taking into consideration the above mentioned specific features.

2. Experimental

Polypropylene of the industrial production mark Kaplen 01030 was used as a matrix polymer and multilayered CNT, having specific surface of 130–150 m^2/g, layers number of 20–30 and external diameter of 20–30 nm were used as nanofiller. The content of CNT was varied within the range of 0.15–3.0 mas %.

PP/CNT nanocomposites were prepared by components mixing in melt on the twin-screw extruder Thermo Haake model Reomex RTW 5567, produced in Germany. Mixing was performed at the temperature of 463–503 K and screw speed of 150 rpm during 5 min. Specimens for tension tests in the form of two-sided spades with the sizes according to GOST-12423-66 were produced by casting under pressure method on the casting machine Test Samples Molding Apparatus RR/TS MP produced by Ray-Ran (Taiwan) at the temperature of 503 K and the pressure of 8 MPa [4].

Mechanical uniaxial tension tests were carried out on the universal testing apparatus Gotech Testing Machine CT-TCS, made in Germany, at the temperature of 293 K and the strain rate of $\sim 2 \cdot 10^{-3}$ s^{-1}.

3. Results and Discussion

The known equation [5] was used to estimate the nanofiller (CNT) content φ_n:

$$j_n = \frac{W_n}{r_n} \qquad (1)$$

where W_n is CNT mass content, r_n is CNT density, estimated according to the equation [3]:

$$r_n = 0.188(D_{CNT})^{1/3} \qquad (2)$$

where D_{CNT} is nanotubes diameter.

In Fig. 1 the experimentally received dependence of reinforcement degree E_n/E_m (E_n and E_m are elasticity moduli of the nanocomposite and matrix polymer, respectively) on filling volume degree j_n is shown. As one can see, at very small j_n values of the order of 0.015 the indicated dependence reaches plateau with small E_n/E_m values about 1.20. Let us note that such magnitudes of reinforcement degree at $j_n \approx 0.06$ are typical of microcomposites, *i.e.* polymer composites with filler of micron sizes [6]. Let us consider the reasons of such behaviour of PP/CNT nanocomposites.

Within the framework of percolation model the estimation of E_n/E_m value can be performed by the following relationship [3]:

$$\frac{E_n}{E_m} = 1 + 11(j_n + j_{if})^{1.7} \qquad (3)$$

where j_{if} is interfacial regions relative fraction, which in CNT case is connected with j_n value as follows [3]:

$$j_{if} = 2.86 j_n b \qquad (4)$$

where b is the parameter characterizing interfacial adhesion level in polymer composites [7].

The parameter b allows to clear gradation of interfacial adhesion level. Hence, the condition $b = 0$ means interfacial adhesion absence; $b = 1.0$ denotes perfect (by Kerner) adhesion; and the condition $b > 1.0$ defines nanoadhesion effect [8]. Let us note that for polymer microcomposites with different fillers and matrix polymers b variation makes up ~ -0.19–1.39 [7].

The parameter b calculation according to the Eqs. (3) and (4) shows its reduction from 5.09 to 0.21 in the range of j_n=0.003–0.060 (Fig. 2). As follows from the data of Fig. 2, CNT contents increase in the studied nanocomposites results in qualitative changes of interfacial adhesion level: at $j_n \leq 0.020$ the nanoadhesion effect is observed; at $j_n \approx 0.025$ the perfect (by Kerner) adhesion is reached; and at $j_n > 0.030$ $b \rightarrow 0$.

The authors [9] considered three main cases of the dependence of reinforcement degree E_n/E_m on nanofiller volume contents j_n. Although the indicated treatment was applied to particulate-filled polymer composites, its application to the studied nanocomposites is of a definite interest as well. There are the following main types of the $E_n/E_m(j_n)$ dependences:

1) perfect adhesion between nanofiller and polymer matrix, described by Kerner's equation, which can be approximated by the following relationship:

$$\frac{E_n}{E_m} = 1 + 11.6 j_n - 44.4 j_n^2 + 96.3 j_n^3 \qquad (5)$$

2) zero adhesional strength at large friction coefficient between nanofiller and polymer matrix, which is described by the equation:

$$\frac{E_n}{E_m} = 1 + j_n \qquad (6)$$

3) complete absence of the interaction and ideal sliding between nanofiller and polymer matrix, when composite elasticity modulus is practically determined by polymer cross-section and is connected with filling degree by the equation:

$$\frac{E_n}{E_m} = 1 - j_n^{2/3} \qquad (7)$$

In Fig. 1 (curve 3) theoretical $E_n/E_m(j_n)$ dependence, calculated according to the Eq. (5), is adduced. Its comparison with the experimentally obtained $E_n/E_m(j_n)$ dependence (curve 1) shows that at $j_n = 0.003–0.015$ (the nanoadhesion effect realization) the experimental E_n/E_m values exceed the theoretical reinforcement degree; at $j_n \approx 0.020$ these magnitudes are equal (as it follows from the data of Fig. 2, at the indicated filling degree $b = 1.0$, *i.e.* perfect adhesion is realized); and at $j_n > 0.020$ theoretical reinforcement degree is higher than the experimental one, which is due to further reduction of interfacial adhesion level at j_n growth (Fig. 2).

Let us consider the reasons of sharp reduction of interfacial adhesion level, characterized by the parameter b, at CNT volume contents growth. CNT orientation factor h is determined as follows [10]:

$$j_{if} = 1.09h \qquad (8)$$

where interfacial regions relative fraction j_{if} can be calculated with the aid of the Eq. (3).
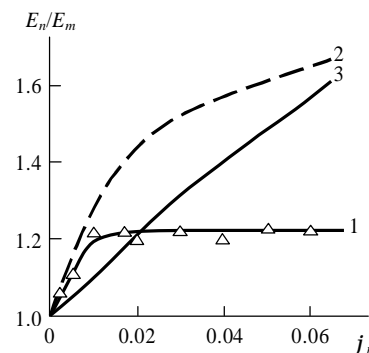

Fig. 1. Dependences of reinforcement degree E_n/E_m on nanofiller volume contents j_n: the experimental data for PP/CNT (1) and LDPE/CaCO$_3$ nanocomposites (2), theoretical calculation (3) according to the Eq. (5)
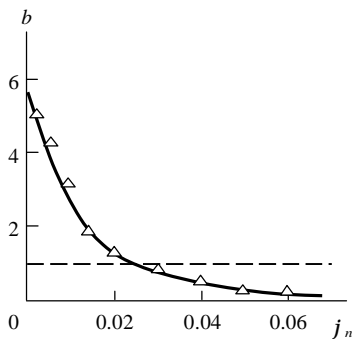
Fig. 2. Dependence of parameter b on CNT volume contents j_n for PP/CNT nanocomposites. The horizontal shaded line shows perfect adhesion level ($b = 1$)
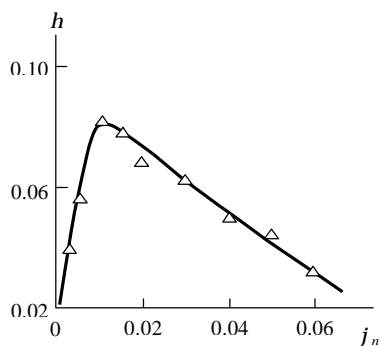

Fig. 3. Dependence of CNT orientation factor h on their volume contents j_n for PP/CNT nanocomposites

In Fig. 3 the dependence of orientation factor h on filling volume degree j_n for PP/CNT nanocomposites is adduced, which has pronounced extreme character with the maximum at $j_n = 0.010$–0.015. Such $h(j_n)$ dependence assumes (together with similar behaviour of other properties for the studied nanocomposites – yield stress s_Y, impact toughness A_p, *etc*. [4]) the common feature, having statistical character: first periodic (ordered) behaviour is observed, which is close to a sigmoid one with period doubling and then transition to chaotic behaviour takes place. Such behaviour is typical of synergetic systems [11] and was observed for phenilone/CNT nanocomposites [12]. However, the latter were processed in rotating electromagnetic field, which essentially reduces the nanotubes aggregation degree. Quantitatively this effect is expressed in maximum displacement from $j_n = 0.015$ for PP/CNT nanocomposites up to $j_n = 0.064$ for phenylone/CNT nanocomposites [3, 12]. In addition, reinforcement degree for the first from the indicated nanocomposites is less than for the second ones: $E_n/E_m = 1.223$ and 1.416, respectively. It is significant that the second value is reached simply at the expense of larger value of j_n at

practically equal h magnitudes. Hence, CNT periodic behaviour consists in their partial orientation in polymer melt and chaotic behaviour means CNT tangled coils formation with final value $h = 0$ [12]. Therefore, the stated above results suppose that the condition $E_n/E_m \approx$ $\approx 1.22 = $ const for PP/CNT nanocomposites at $j_n \geq 0.015$ (Fig. 1) is defined by j_n increase compensation at the expense of j_{if} reduction (Eq. (3)), due to CNT aggregation or η decreasing (Eq. (8)). In its turn, j_{if} decreasing is due to reduction of interfacial adhesion level, characterized by the parameter b, in virtue of the same CNT aggregation.

It is often supposed [13] that at present CNT are the most promising nanofillers for polymer nanocomposites production. A similar opinion was repeatedly stated earlier in respect of organoclay [14]. In Fig. 1 the $E_n/E_m(j_n)$ dependence is adduced, where j_n is calculated according to the Eqs. (1) and (2), for particulate-filled low density polyethylene/calcium carbonate (LDPE/CaCO$_3$) nanocomposites [15]. As follows from the $E_n/E_m(j_n)$ dependences comparison for PP/CNT and LDPE/CaCO$_3$ nanocomposites, the advantage of the latter is obvious. However, it is impossible to assert that some type of nanofiller has some definite advantages. Final properties of polymer nanocomposites are defined by a set of parameters: interfacial adhesion level, nanofiller aggregation degree, correct choice of polymer matrix, *etc*. [3]. From technological and economic standpoint the most attractive disperse particles are those that are cheap, easily processed by a binding agent, and simply dispersed. At the same time, presently it seems unlikely to obtain exfoliated organoclay at $W_n > 3$ mas %. Still it is more difficult to obtain separate CNT, not in the form of tangled coils, which, as was indicated above, are in addition very expensive. Therefore, wide-scale application of polymer/CNT nanocomposites as engineering materials in the nearest future seems unlikely. This, however, does not exclude their usage for specific applications [2, 14, 16]. Theoretical prospects of CNT application in the indicated capacity are also obvious. So, at the obtained in the present paper (and, hence, real ones) the largest values of $h = 0.083$, $b = 5.09$ and at $j_n = 0.060$ ($W_n = 3$ mas %) elasticity modulus of PP/CNT nanocomposites can reach ~ 9210 MPa. However, the same value of elasticity modulus can be obtained for nanocomposites on the basis of PP taking into account the conditions $j_{if} = 1.225\varphi_n b$ [3] and $b = 5.09$ at disperse nanofiller with diameter of 20 nm containing 6.3 mas % only or with diameter of 50 nm – 8.0 mas %. It is obvious that technologically and economically the last variant is more preferable.

Let us also note in conclusion another important methodological aspect. As distinct from widely used micromechanical models [5, 6], none of the adduced

above equations used nanofiller elasticity modulus as a parameter. Such approach is typical of percolation [17] and fractal [18] polymer composites (nanocomposites) reinforcement models. The indicated treatment is confirmed in practice: exceptionally high elasticity modulus of CNT [14] does not give them any advantage in comparison with organoclay or disperse nanofiller (Fig. 1).

4. Conclusions

The results obtained in the present paper show the carbon nanotubes aggregation (tangled coils formation) begins with their very small contents and strongly restricts elasticity modulus enhancement of the obtained nanocomposites. The offered model does not take into consideration nanofiller elasticity modulus and shows that the general properties of polymer nanocomposites are defined by interfacial adhesion (nanoadhesion) level, nanofiller aggregation degree, and polymer matrix choice. The performed theoretical estimations show high potential of polymer nanocomposites.

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СИНЕРГЕТИКА УТВОРЕННЯ СТРУКТУРИ І ВЛАСТИВОСТІ НАНОКОМПОЗИТІВ ПОЛІПРОПІЛЕН/ВУГЛЕЦЕВІ НАНОТРУБКИ

Анотація. Показано, що агрегація (утворення переплутаних клубків) вуглецевих нанотрубок починається при дуже малому їх вмісті. Цей чинник значно понижує ступінь підсилення нанокомпозитів полімер/вуглецеві нанотрубки. Проведено оцінювання основних параметрів, які впливають на модуль пружності вказаних нанокомпозитів. Теоретичні розрахунки показали високий потенціал нанокомпозитів, наповнених нанотрубками.

Ключові слова: нанокомпозит, вуглецеві нанотрубки, агрегація, ступінь підсилення, міжфазова адгезія, синергетика.