Polymer nanocomposites: Problems, preparation, mechanical properties

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Abstract

The main target of this review article is to try to find the reasons for the drastic difference between expected and observed mechanical properties of polymer nanocomposites prepared via blending the matrix and the nano-reinforcement. Additional target is to recommend thereafter ways for solving of this problem. Based on the published materials the conclusion is drawn that the main reason for this discrepancy is the poor dispersion resulting in formation of particles with sizes in the micrometer but not in nanometre range. For this reason, it is assumed further that these nanocomposites hardly exist. Since currently are missing techniques and instrumentation for a proper dispersion of the reinforcement to single nanoparticles, it is recommended to avoid the dispersion step during manufacturing of polymer nanocomposites. Two techniques are described for this purpose, representing application of the rather new concept of "converting instead of adding" for preparation of polymer nanocomposites. Copyright © 2018 VBRI Press.

Keywords: polymer nanocomposites, mechanical properties, reinforcement dispersion, concept of converting instead of adding

Introduction

During the last decades revolutionary changes happened in the material science – a new type of materials were created - the nanomaterials. *Nanomaterials* are materials with morphological features on the nanoscale, and their special properties are stemming from their nanoscale dimensions, which usually are defined as smaller than a one tenth of a micrometer in at least one dimension. Recently [1], the European Commission offered a more precise definition, namely, 50% or more of the particles in the number size distribution are in the size range 1–100 nm. A common characteristic feature of all nano-size materials, regardless of their chemical composition and method of manufacturing, is the extremely high ratio of surface area to volume. For example, 1 kg of particles of 1 mm^3 has the same surface area as 1 mg of particles of 1 nm^3. The natural tendency to reduce this free surface is the driving force for agglomeration of nanoparticles in larger formations approaching the micrometer range.

Although nanoparticles are generally considered a discovery of modern science, they actually have a very long history. Nanoparticles have been used by artisans as far back as the ninth century in Mesopotamia for generating a glittering effect on the surface of pots.

A milestone in the development of nanomaterials was the discovery of carbon nanotubes, which usually is credited to Iijima [2]. It turned out that carbon nanotubes are the strongest material ever created – with an elastic modulus in the terapascal range carbon nanotubes (CNTs) overcome any known material. The idea to use CNTs as reinforcement of plastics arose immediately because simple model calculations demonstrated thatsmall amounts of this reinforcement will result in some 10-fold increase of the elastic modulus, and so started the "era of polymer nanocomposites".

Problem: why the mechanical performance of polymer nanocomposites does not justify the expectations?

The expectation formulated two decades ago, that the most common polymer composites comprising about 30% glass fibers will be replaced by nanocomposites having as reinforcement only 2–5 wt. % nano-size minerals turned out to be elusive.

Discussing the mechanical behavior of polymer nanocomposites it should be stressed that an improvement of 20% (for tensile strength) and 50% (for the modulus of elasticity) is quite typical for all polymer nanocomposites [3]. According to Bousmina [4], only in exceptional circumstances can one observe an improvement greater than 30% in the mechanical performance of nanocomposites. More specifically, Zhang *et al.* [5] studied thoroughly the case of polypropylene (PP)/SiO_2 nanocomposites in which nanoparticles have been coated by various polymers to improve the interfacial adhesion. They reported mechanical properties (Young's modulus and tensile strength) only 20 – 25% higher than those of the neat PP [5].

The above conclusions were supported by the statements of Schaefer and Justice in their review "How Nano Are Nanocomposites?" [6]: *"Composite materials loaded with nanometer-sized reinforcing fillers are widely believed to have the potential to push polymer mechanical properties to extreme values. Realization of anticipated properties, however, has proven elusive".*

As mentioned above, such systems have attracted enormous interest from the materials community because they theoretically promise substantial improvement of mechanical properties at very low filler loadings. In addition, nanocomposites are compatible with conventional polymer processing, thus avoiding costly layup required for the fabrication of conventional fiber-reinforced composites. The appeal of nanocomposites is illustrated by considering single walled carbon nanotubes (SWCNTs). With tensile moduli in the terapascal range and lengths exceeding 10 μm, simple composite models predict order-of-magnitude enhancement in modulus at loadings of less than 1%.

"Introductory paragraphs similar to the above can be found in hundreds of nanocomposite papers. With the exception of reinforced elastomers, nanocomposites have not lived up to expectations. Although claims of modulus enhancement by factors of 10 exist, these claims are offset by measurements that show little or no improvement. The lacklustre performance of nanocomposites has been attributed to a number of factors including poor dispersion, poor interfacial load transfer, process-related deficiencies, and others" [6].

And finally, let mention in this respect the statement in a very recent review on the practical applicability of polymer nanocomposites [7]: "Initial developments of nanocomposite thermosets focused on high aspect ratio nanoparticles such as nanoclays, carbon nanotubes and more recently graphenes. Generally, these systems showed 10 − 35 % improvement in mechanical properties with 0.2 − 5 wt. % filler. However, the translation of these improvements to prepregs or laminates proved to be difficult due to processing issues, including extremely high viscosity, nanoparticles filtration, nanoparticles agglomeration, and void formation."

It seems rather realistic to assume that polymer nanocomposites prepared via melt blending of the two basic components, the matrix and the reinforcement, are characterized by a maximum improvement of their mechanical properties by 30 − 35% as compared with the respective neat isotropic matrix. Such a result is quite far from the expected 10-fold (at least!) improvement.

An interesting question regarding the reasons for this drastic discrepancy arises.

The concept of polymer nanocomposites, that is, the expectation that using 1−5% of nanofiller instead of the common 30–40%, it will be possible to realize improvements of magnitude of order as compared with the traditional composites materials as well as to enhance the environmental impact of these materials failed for the following reasons:

(i)   Poor dispersion
(ii) Poor interfacial load transfer
(iii) Process-related deficiencies
(iv) Poor alignment
(v)   Poor load transfer to the interior of filler bundles
(vi) The fractal nature of filler clusters.

Do polymer nanocomposites prepared via blending a polymer with nanomaterial really exist?

Such question sounds rather provocative but if we remember the criteria according to which the composite materials are categorized, we will see that the question is justified. Depending on the sizes of the reinforcing filler we distinguish between *macrocomposite* (the common ones), *microcomposites*, when the sizes are in the micrometer range and *nanocomposites* if the single reinforcing particles are nano-size particles, i.e. with dimensions below 100 nm or around this size.

Dealing with this "terminological" issue, it seems important to remind how the polymer nanocomposites are prepared. The most common practice is to blend a polymer (the matrix) with nano-size material (reinforcement) and to add to the title of paper the modern word "nanocomposite". In rare cases attempts are undertaken to determine the degree of dispersion and if this is done, it is by means of electron microscopy. Usually, 2 − 3 micrographs are shown comprising a couple of nano-size particles, which demonstrate how these particles look but, by no means, they offer any information about their amount in the sample. The question regarding the degree of dispersion still remains without answer. Such information can be obtained by using scattering techniques – X-ray, neutron scattering, etc. On this important detail is also stressed in the recent review on polymer nanocomposites [7].

The electron microscopes reveal also rather large aggregates of nanoparticles with sizes sooner closer to the micrometer range rather than to the nanometre sizes. Their existence is to be expected taking into account the extremely strong tendency of nano-size material to reduce the surface energy via agglomeration. The question is if these aggregates dominate in the sample. The answer can be found if we return to the scattering techniques, for example light scattering.

There are polymers which are completely transparent, i.e. they let the light trough on 100% as, for example, atactic poly(methyl methacrylate) (at-PMMA), atactic polystyrene (at-PS) and, to some extent, polycarbonates (PC) and polyarylates (PAr) do. They can be used as a matrix for preparation of nanocomposites via blending with nano-size fillers.

The nanomaterials of inorganic origin have typical sizes below 100 nm and in many cases around 2 − 5 nm. If the dispersion during mixing with the matrix is a good one, i.e., up to single nanoparticles, the transparency should not be different from that of the matrix, that is, the

transmission of the light has to be 100%. This situation is due to the known fact that light scattering can be observed only if particles have sizes in the range of the size of the wave length of the used light, which for the common light is 500 – 600 nm.

Let look at the results of such studies. Nanocomposites have been manufactured from completely transparent at-PMMA (100% transmission of the light) and nano-size ZnO (particles of 75 nm in concentration 1 wt. %). The used light was with wave length $\lambda = 600$ nm. The measured amount of transmitted light is only 2 % but it increases up to 50 % if the concentration of the filler drops to 0.01 % [8].

Similar nanocomposite has been prepared using the same matrix and ZrO_2 with particles size of 4 nm and concentration of 15 %. The transmission of the light ($\lambda = 600$ nm) was 80 % [9]. Even finer ZnO filler (2.3 nm) in concentration of 0.5 % showed 90 % transmission of the light [10].

Practically the same are the results of another completely transparent matrix, the at - PS - when as reinforcement is used CeO (size 20 nm, concentration 20 wt. %) the light transmission decreases to 75 % [11]. In cases when as matrix is used PC the observed results are similar. For example, whiskers of AlO_2 in concentration of 2 wt. % cause reduction of light transmission up to 80 % [12], while Al_2O_3 (size 96 nm, concentration 1 wt. %) shows 50 % transmission of the light [13].

It should be mentioned that in all cited cases the thickness of the samples subjected to light transmission measurement has been between 1 and 4 mm.

The observed [8-13] serious decrease in light transmission of the cited nanocomposites as compared with their completely transparent matrices leads to the conclusion that in these blends the dispersed particles by far are not nano-sized. Taking into account the fact that they scatter the common light ($\lambda = 500 - 600$ nm), their sizes should be in the same range, which, in many cases, is some 100 times larger than the real sizes of the single particles introduced to the polymer matrix.

At such a situation it is hardly correct to call these composites "nanocomposites" because they, as a matter of fact, belong to the category of microcomposites. If we agree with this statement a quite important conclusion can be derived – the answer of the very basic question about the drastic difference between expected and observed mechanical properties of the polymer nanocomposites prepared via blending matrix and reinforcement. They do not justify the expectations derived for nanocomposites because they are not nano - but microcomposites. The situation is really interesting because it could be considered from its reverse side – the lack of agreement between observed and predicted mechanical properties support the conclusion that these composites are not of nano type. And this can be proven if we succeed to prepare real polymer nanocomposites and measure their mechanical properties.

Solution of the problem: Avoiding the dispersion as manufacturing step

Nowadays a rather large number of nano-size materials are available and nevertheless the preparation of true nanocomposites is not an easy task. The basic problem in manufacturing of polymer nanocomposites is the dispersion of the reinforcing component to single nanoparticles in the matrix material. Due to the inherent property of the nano-size materials, namely, the extremely high specific surface, they tend to agglomerate and their further dispersion in the matrix component is practically impossible. In this respect, it seems useful to cite here the opinion of Greiner and Wendorff [14] expressed in their excellent review of electrospinning as a method for preparation of ultrathin fibers and their application as reinforcing material for nanocomposites. After listing the advantages of the electrospun nanofibers as reinforcement over macroscopic fibers as owing to their extremely high aspect ratio, little refraction of light (due to the small diameters) resulting in transparent reinforced matrices, the authors [14] conclude: ''Given the advantages of nanofibers for reinforcement, the number of investigations on this topic is rather small. The main problems, to which there are no convincing solutions yet, are the dispersion of the electrospun nanofiber webs and the control of the nanofiber orientation in the polymer matrix.

The felt-mat structure of the nonwoven is for the most part maintained upon the incorporation of the nanofibers into the matrix. Attempts to disperse single nanofibers from the nonwoven mats using ultrasound, kneaders, or high-speed stirrers have only been marginally successful.

Very similar problems occurred in matrix reinforcement with carbon nanotubes and nanofilaments [15]'' [14].

It appears that currently we do not have reliable tools and/or techniques for a proper dispersion of nanomaterials in polymer melts in order to reach the dispersion degree of single nanoparticles what is the requirement for having true nanocomposites. Obviously, so far such techniques for preparation of these composites are missing we have to create methods free of the dispersion step in the manufacturing process. Such an opportunity is offered by the new concept of "*converting instead of adding*" [16], that is, converting the bulk polymer into nano-size material instead of blending it with nanofillers. In this way it is possible to avoid the practically non-soluble problem of proper dispersion and to create true polymer nanocomposites distinguished by perfect distribution of nanoparticles in the matrix.

The realization of the new concept means that instead to take the two basic composite components, the matrix and the reinforcement, in their final form and blend them, one takes one component only in its final form and during the processing creates the missing second component. For example, starting from blend of two thermodynamically non-miscible polymers, we can convert the minor blend component into nanofibrils playing later the role of

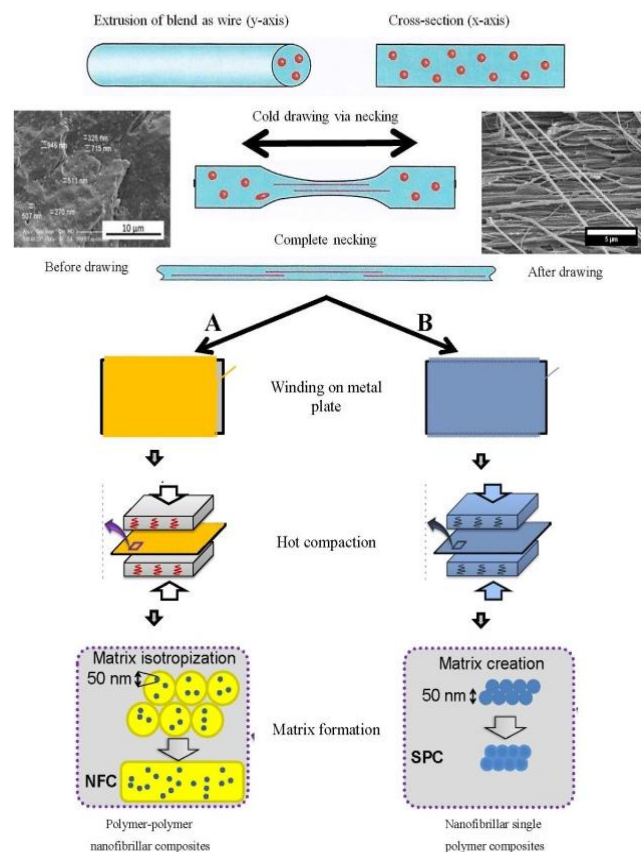reinforcement of the nanofibrillar polymer-polymer composite (PPC).

Fig. 1. Manufacturing of nanofibrillar PPCs (NFC) (Route A) and nanofibrillar SPCs (Route B) via the concept of converting instead of adding.

In the second case, instead of having the matrix in its final form we can use neat polymer nanofibrils and during the subsequent processing to create the missing matrix. This can be done by subjecting the nanofibrils to thermal treatment close but below the temperature of complete melting when a small amount of the same polymer is converted in isotropic matrix (playing the role of binder of nanofibrils). In this way a nanofibrillar single polymer composite (SPC) is prepared.

A characteristic feature of the two approaches is that a perfect distribution of the nano-filler is observed, i.e. each single nanoparticle is surrounded by matrix material and no aggregates of nanoparticles are observed.

The manufacturing process of nanofibrillar PPCs and SPCs is schematically shown in **Fig.1**. It should be noted that this process can be performed on common equipment for polymer processing. The two thermodynamically non-miscible polymers in a usual ratio A/B = 70/30 by wt. are melt blended, extruded and cold drawn as shown on the upper part of **Fig. 1**. Again there, two micrographs of scanning electron microscope (SEM) are added. They demonstrate the drastic morphologic change in the minor component (reinforcement) from spheres (left) to nanofibrils (right). This transition takes place during the

cold drawing via necking. The result so far is preparation of a drawn blend comprising nanofibrils of the minor component.

It seems important to note here that the prepared material is still not a composite material because it would be hardly correct to call the synthetic textile yarns prepared from polymer blends "composites" – both blend components are in a highly oriented state. Additional treatment step is needed in order to convert the dominating (but with lower melting temperature) component from highly oriented into isotropic state. For this purposes the drawn bristle is winded on a metal plate and subjected to compression molding at melting temperature of the matrix polymer A, which has to be at least 40^0C below the melting of the reinforcing polymer B **(Fig. 1, Route A)**. In this way a nanofibrillar polymer-polymer composite is prepared.

For preparation of nanofibrillar single polymer composites one has to select the Route B **(Fig. 1)**, according which from the drawn bristles has to be removed the matrix polymer A using a selective solvent. The rest of nanofibrillar bunch of B has to be winded on a metal plate and compression molded at temperature at least 20^0C below the melting temperature of B **(Fig. 1, Route B)**. This treatment results in creation of small amount of isotropic matrix (binder of nanofibrils **(Fig. 1, Route B)**.

If we analyze the prepared two materials, the PPC and the SPC, by means of SEM, we can get important information regarding the sizes of the reinforcing nanofibrils and, what is more interesting in the current case, the distribution character of the reinforcing nanofibrils in the matrix. Such results for the two materials under discussion are shown in **Fig. 2**.

The photographs taken from the cryofractures perpendicular to the nanofibril orientation **(Fig. 2a and c,** as well as from cryofracture parallel to the nanofibrils orientation **(Fig. 2b)** demonstrate rather homogeneous distribution of the reinforcing nanofibrils in the polymer matrix, i.e. practically, no aggregates of nanofibrils can be observed. Such a situation is quite different from the case of polymer nanocomposites prepared via blending of the two starting components as demonstrated in the previous paragraphs.
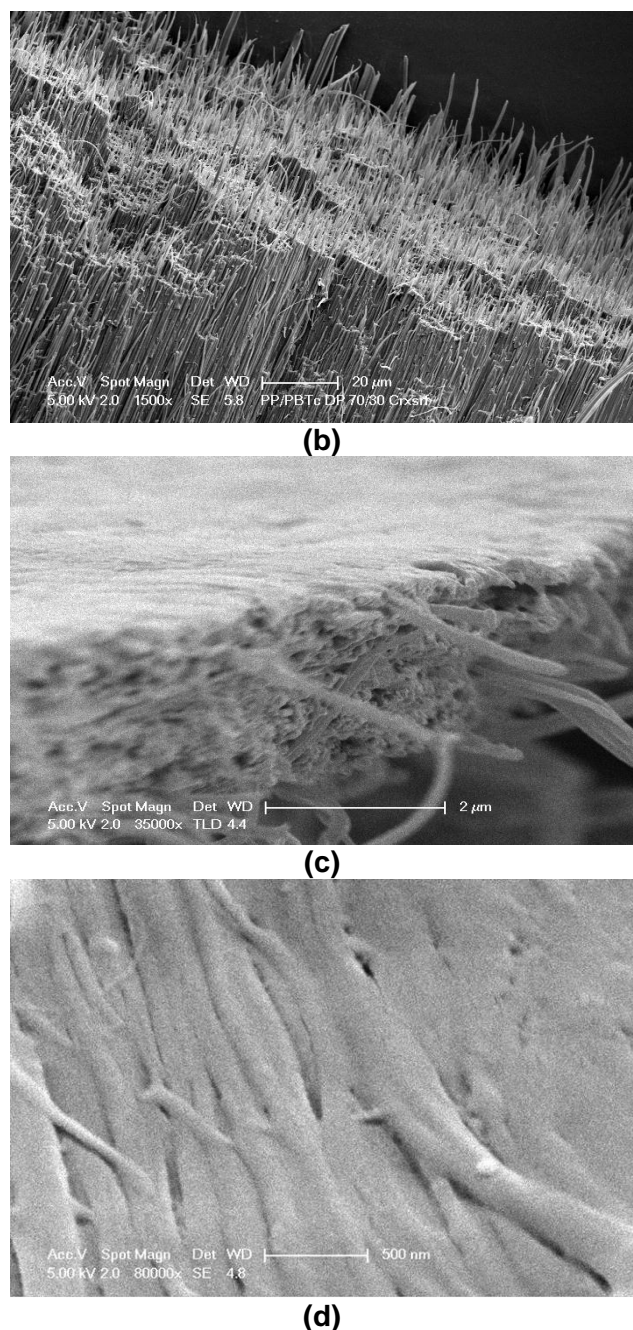

(a)

Fig. 2. SEM micrographs of polypropylene/poly(buthylene terephthalate) (PP/PBT = 70/30 by wt.) nanofibrillar polymer-polymer composite (a and b) and PET nanofibrillar single polymer composite (c and d): a) and c) – cryofracture perpendicular to the nanofibril orientation, b) – cryofracture also parallel to the nanofibrils orientation, and d) – the surface of the SPC film shown in c).

Mechanical performance of nanofibrillar polymer-polymer and single polymer composites

The nanofibrillar polymer–polymer composites, prepared according to the concept of converting instead of adding demonstrate superior mechanical performance. Let mention two examples, the linear low density polyethylene/poly(vinylidene fluoride) (LLDPE/PVDF) [17] and the polypropylene/poly(buthylene terephthalate)

(PP/PBT) [16]. In both cases the two components are taken in weight ratio 70/30. The observed improvement in the elastic modulus in the first case is 165 % and in the second case – 45 % while the improvements in the tensile strength are much higher, 230 % in the first case and 190 % in the second.

This impressive mechanical performance of the nanofibrillar polymer-polymer composites originates from the very high aspect ratio of nanofibrils, their better adhesion then the mineral fillers to the matrix and mostly from the perfect distribution of nanofibrils in the matrix.

Even higher are the reinforcing effects in tensile experiments of the true nanofibrillar (diameter of nanofibrils between 10 and 250 nm) SPCs, prepared via one-constituent approach. The comparison is done with isotropic film of the same polymer prepared via compression molding with a thickness similar to that of the SPC samples.

For the nanofibrillar single polymer composite based on PVDF the improvement in elastic modulus is 40 % and of the tensile strength - 330 % [16], for poly(ethylene terephthalate) (PET) – 350% and 300 %, respectively [18], for LLDPE - 112 % and 325 %, respectively [19], and for PP - 70 % and 440 %, respectively [19].

The improvements in the tensile mechanical properties of all SPCs so far reported [20 – 25], and particularly the superior mechanical properties of the new nanofibrillar SPCs [16-19] prepared by hot compaction using only one constituent are evident. What could be the reason for this impressive mechanical performance? There are at least four reasons: (i) in the current SPCs the reinforcing constituent dominates strongly, and has much better mechanical properties when compared with the isotropic matrix of the same polymer, (ii) excellent adhesion between matrix and reinforcement because they have the same chemical composition, (iii) better orientation of the macromolecules in nanofibrils as compared to that in microfibrils and textile filaments of the same polymer, and (iv) in the test specimen of SPCs the nanofibrils are uniaxially aligned and the testing has been performed so far in the drawing direction only.

Conclusions and outlook

Nowadays it seems generally accepted that the concept of polymer nanocomposites did not justify the expectations – a drastic difference in mechanical properties between the theoretically derived and the experimentally obtained results is observed. The most probable reason for this discrepancy is the poor dispersion – reinforcements are not the single nanoparticles but their aggregates with sizes in the micrometer range. This situation is since currently there are not reliable techniques for proper dispersion of nanomaterials aggregates into polymer matrix. For this reason, so long such techniques are missing we should avoid the dispersion step in the preparation of true polymer nanocomposites as the concept of converting instead of adding does.

Two techniques being the essence of the new concept are described, where instead to take the matrix and the reinforcement in their final form and blend them one takes one component only and during the processing creates the missing second component [16-18, 24-27].

Both techniques are free of the dispersion step and, what is more important, one always observes a perfect distribution of the reinforcing nanomaterial in the polymer matrix, i.e. each nanofibril is individually surrounded by the matrix polymer and no aggregation is observed on the scanning electron micrographs. In addition, both type of polymer nanocomposites, the nanofibrillar polymer-polymer composites and the nanofibrillar single polymer conposites are distinguished by excellent mechanical performance – up to 300 – 400 % improvement in tensile strength and modulus, i.e. up to 10 times higher than polymer nanocomposites prepared via blending of matrix and reinforcement.

The properties of these polymer nanocomposites, prepared by means of dispersion-free methods and characterized by perfect nanoparticles distribution in the matrix, can be further improved attacking the rest of their drawbacks as: poor interfacial load transfer, process-related deficiencies, poor alignment, and poor load transfer to the interior of filler bundles.

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