Polymer Composites with Surface Modified SiO$_2$ Nanoparticles: Structures, Properties, and Promising Applications

O. A. Serenko* and A. M. Muzafarov

Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia
**e-mail: oserenko@yandex.ru*
Received September 21, 2015

Abstract—Data from recent studies of polymer composites with nanosized silica particles are considered. A comparative analysis of current approaches to the description of concentration changes in the glass-transition temperatures of these systems is performed. The morphology of the surface layer in materials with nanoparticles and its effect on the characteristics of materials are discussed. The surface layer of a composite is represented as a shell including both the polymer and the external part of the filler. A conditional division between the functions of the external layer and the nanoparticle core makes it possible to determine in a first approximation which characteristics of the matrix and the filler have an effect on the properties of nanocomposites.

Polymer-based nanocomposites are promising materials for the design of new engineering prototypes and multipurpose functional materials. The range of their possible applications is so wide (from packaging materials to car bumpers and from drug products to optoelectronic devices) that it is difficult to find a field of industry or engineering where these composites are not in demand. The great amount of attention form researchers and engineers to these innovative composites is due to the possibility to obtain materials with unusual properties that cannot be attained via the addition of conventional microsized fillers to a polymer.

The research papers, reviews, and monographs dedicated to these materials number in the ten thousands. For example, one can find more than four thousands references for 2015 at the ScienceDirect Web site alone. Most of the publications are dedicated to applied problems, such as the preparation of nanocomposites and the study of their properties via different instrument-based methods. An empirical approach to new composite materials is certainly efficient, especially in those cases where researchers succeed in achieving the expected results. However, researchers have to deal with a more difficult case when no positive changes are observed after the addition of a nanosized filler, and there are quite a lot of such cases, although not all of them are mentioned in scientific publications.

Likewise, the attempts to analyze the causes of successful and failed experiments are frequently encountered. Unfortunately, most of them generalize the facts obtained for different materials, a circumstance that considerably decreases the objectivity level of the analysis data and generalizations [1–15]. Numerous "discrepancies" in the published works restricted us to selection of the most common nanosized filler–polymer pairs and forced us to use the results from the study of model systems containing nanoparticles with well-controlled surfaces and, finally, to focus on detecting the factors defining the positive or negative effect due to the addition of a nanosized filler to a polymer.

According to the current classification of nanoparticles, they are divided into three types: 2D (for example, nanoclays), 1D (carbon nanotubes), and 0D (fullerenes, silica) [2, 16]. The polymers containing one of the above-mentioned nanoparticle types can be regarded as an individual class of nanocomposites with their unique features caused by the filler shape [2, 3, 14–17]. To avoid the effect of nanoparticle shape on the properties of a composite material, we confined ourselves to the analysis of systems with 0D nanoparticles. Moreover, to exclude the possible effect of a different chemical composition or the particle nature on the properties of the material as a whole, the review will consider studies where different modifications of silica were used as nanosized fillers.

Silicon dioxide (SiO$_2$) is a common filler widely used for rubbers, thermoplastics, and thermosetting materials. The addition of SiO$_2$ to the formulation of a polymer material is known to increase the modulus of elasticity, strength, heat and fire resistances, wear resistance, insulating properties, etc. [8, 18]. After the transition from micro- to nanosized SiO$_2$ particles, the composite materials can acquire new unique proper-

Table 1. Changes in glass-transition temperatures ΔT_g of the systems based on amorphous glassy polymers and nanosized silica particles

Polymer	Solvent	Particle size, nm	Finishing agent	Size of aggregates in polymer, nm	Filler concentration	ΔT_g, °C	Reference
			Mixing of a polymer solution with a suspension of nanoparticles				
PS	2-Butanone	10−15	no	−	up to 20 vol %	+(1−2)	[26]
	2-Butanone	14 ± 4	no	−	5 wt %	−4	[27, 28]
	Dimethylacetamide	5.2	no	60−120	up to 20 vol %	+6	[29]
	Toluene	12	no	−	up to 5 vol %	+5	[30]
		20	″	−	up to 7.5 vol %	+7	[30]
		40	″	−	15 vol %	+11	[30]
	N,N-Dimethylfor-mamide	28.7 ± 0.3	Trimethoxyphenylsilane	up to 200	10 vol %	+2	[31]
	Toluene	7	Hexamethyldisilazane	up to 60	up to 30 wt %	+6	[32]
PMMA (75×10^3)	2-Butanone	14 ± 4	no	−	1 wt %	−1	[33]
				−	20 wt %	0	
PMMA (3×10^5)	Methanol	−	no	up to 250	up to 30 wt %	0	[34]
PMMA (6×10^5)	N,N-Dimethylfor-mamide	28.7 ± 0.3	Trimethoxyphenylsilane	up to 200	1 vol %	+ 4	[31]
			Mixing of a polymer melt with nanoparticles				
PS	16		Dimethyldichlorosilane	100−300	up to 4 wt %	0	[71]
PC	40		3-(Trimethoxysilyl)propyl methac-rylate	up to 600	5 wt %	+5	[72]
PMMA	16		no	50−300	up to 5 wt %	+3	[73]
	100 and 117		(3-Aminopropyl)triethoxysilane	n/a	3 wt %	−3	[74]
	15±5		(γ-Glycidyloxypropyl)trimethox-ysilane	85−200	up to 5 wt %	0	[75]
	16		no	up to 200	up to 5 wt %	+(4−5)	[76]
Polysulfone	11		no	50−100	up to 10 wt %	+2	[77]
Poly(butylene succinate)	20		Octadecyltrichlorosilane	up to 300	10 wt %	+(3−4)	[78]

ties, such as transparence, UV resistance, and surface hydrophobicity, in addition to the above-mentioned characteristics [5, 8, 15].

Polymer−nano-SiO$_2$ mixtures are prepared through several processes: namely, mixing a polymer solution or melt with a suspension of nanoparticles, the sol−gel technique (in situ filling during which a polymer is mixed with a nanoparticle precursor), and in situ polymerization of a polymer in the presence of a filler.

All of the mentioned methods and their variations have been considered in detail in reviews and monographs [2, 4, 5, 8, 15, 19−22]. Note that the preparation of nanocomposites is accompanied by the necessity to solve a complex problem: providing a uniform distribution of nanosized particles over the bulk of a

polymer [4, 11, 12, 15, 23−25]. High surface energies of nanoinclusions favor their agglomeration.

It is more convenient to begin the analysis of data from various authors with systems obtained via mixing a of polymer solution with silica nanoparticles whose surfaces have not been pretreated with any modifiers (finishing agents). During preparation of the mixture via the above-mentioned method, additional dispersion procedures, such as shaking and ultrasonic treatment, are used to improve the quality of mixing. Let us use as the comparative characteristic glass-transition temperature T_g, which, on the one hand, predetermines the relaxation behavior, modulus of elasticity, gas permeability, etc, and, on the other hand, reflects the problems existing in this field of polymer materials science. Table 1 gives the T_g values for PS- and

PMMA-based systems. The data from various authors [26−34] are quite contradictory. In one case, the glass-transition temperatures of materials based on the same polymer increase with an increase in the nanoparticle content and, vice versa, decrease in other cases. The increase or decrease in T_g is observed for both the nonpolar polymer (PS) and the polymer containing polar groups (PMMA).

Studies [6, 27, 28, 35, 36] proposed an approach to explain the change in the glass-transition temperatures of nanocomposites that can be formulated in a simplified form as follows. If a polymer wets the nanoparticle surface, T_g of the composite will increase with an increase in the nanoparticle content and decrease in the opposite case. The main facts supporting the validity of the proposed approach are results from the study of glass-transition points of thin polymer films. The glass-transition temperature of a supported polymer was found to increase with a decrease in the thickness of the polymer layer. In the study of free thin films, the glass-transition temperature of a polymer increased with an increase in its film thickness. Indeed, according to the data of [37], the glass-transition temperature of PMMA adsorbed on the surfaces of untreated silica nanoparticles can be 56°C higher than that of the bulk polymer. In addition, an increase in the glass-transition temperature of PMMA by an average of 10°C near the surfaces of SiO$_2$ nanoparticles prefinished with (3-aminopropyl)dimethylethoxysilane was reported in [38].

According to [27, 28, 35, 36], with consideration for the hydrophilicity of the SiO$_2$ particle surface, the glass-transition temperatures of composites based on polymers containing polar (oxygen-containing) groups must be higher than that of the starting polymer and increase with an increase in the content of the nanosized filler. If a hydrophobic polymer is used for the preparation of a composite, the addition of hydrophilic particles conversely results in a decrease in T_g. The equation describing the change in T_g of a nanoparticle-containing polymer was proposed in [27, 35, 39]:

$$T_g(h) = T_g^{bulk} + \frac{2\xi(T_g(h))}{h}(T_g^{surf} - T_g^{bulk}), \qquad (1)$$

where T_g^{bulk} is the glass-transition temperature of polymer in the bulk, $\xi(T_g(h))$ is the thickness of the surface layer with glass-transition temperature T_g^{surf}; and h is the thickness of the polymer film or the distance between the nearest particles.

The analysis of Eq. (1) shows that, if $T_g^{surf} > T_g^{bulk}$, the glass-transition temperature of a material increases and, vice versa, if $T_g^{surf} < T_g^{bulk}$, its glass-transition temperature decreases with an increase in the concentration of the nanosized filler. Indeed, the

T_g values for the nanocomposites based on PMMA, poly(ethyl methacrylate), and poly(2-vinylpyridine) were higher than those of the starting polymers and increased with an increase in the nanoparticle concentration, whereas the T_g values for the PS−nano-SiO$_2$ systems decreased. The experimental data given in [27, 28, 35, 36] were used in the development of a thermodynamic approach to predict the glass-transition temperatures of nanocomposites [40].

However, as the table shows, such a change in the T_g values of nanocomposites is not a rule. For example, in terms of the concept proposed in [27, 35], it is unlikely that the glass-transition temperature of a composite will increase upon the addition of silica nanoparticles to PS. Nevertheless, in [29, 30], the samples obtained with the use of unfinished silica nanoparticles showed increased glass-transition temperatures. The fact that wetting−unwetting of the nanoparticle surface with a polymer is not a principal factor defining the concentration change in (or constancy of) the T_g values for polymer−nano-SiO$_2$ systems is evidenced also by the data from [41]. Composites based on poly(arylene ether nitrile) (PEN) have been studied as well. Nanoparticles were pretreated with PEN containing pendent carboxyl groups. In its procedural essence, the preliminary treatment of nanoparticles corresponds to adsorption of the polymer onto the silica surface and is an attempt to preform a layer with a higher glass-transition temperature than that o the matrix polymer. The comparison of procedures used in [41] and [37] shows their similarity. Note that the authors of [37] established a significant increase in the glass-transition temperature of the silica-surface-adsorbed polymer layer. However, the T_g values obtained for the PEN-based composites were found to be lower than that of the starting polymer [41].

Another approach to explain the change in T_g of nanocomposites is based on the assumption that the nanoparticle surface possessing excess surface energy seems to attract the matrix macromolecules to itself, thereby dramatically decreasing their segmental mobilities [42]. The properties of this immobilized polymer layer are described through the use of the concept of a "rigid amorphous phase" or "glassy polymer layer" [17, 29, 43−50] whose devitrification occurs at higher temperatures. The content of the "bound polymer layer" increases with an increase in the filler concentration and the molecular mass of the polymer [17]. In [31, 42], the reinforcing effect of nanoparticles was observed in the case when the distance between their surfaces was comparable with $2R_g$, where R_g is the radius of gyration of the polymer chain. While the former approach to predict the sign of the shift in T_g of nanoparticle-containing polymer systems can be regarded to a greater degree as semiempricial, the latter approach is confirmed by the data from the computer simulation [51−53].

In accordance with the foregoing, the addition of nanoparticles to a polymer will result in an increase in T_g of the system. The experimental evidence for the assumption that the immobilized layer of the matrix polymer forms is the data from studies reporting two glass-transition temperatures of nanocomposites, one of which corresponds to the surface layer, while the other corresponds to polymer devitrification in the (polystyrene–polybutadiene)–SiO$_2$ [54], polydimethylsiloxane–SiO$_2$ [55], polyvinylpyrrolidone–SiO$_2$ [56], or PVA–SiO$_2$ block [57].

However, according to the example of the polyvinyl acetate–SiO$_2$ composite, the authors of [58] provided convincing evidence that the SiO$_2$ nanoparticles have no effects different from those of usual microparticles; both the permanence of the glass-transition temperatures of materials and the absence of two glass-transition points for the matrix polymer were especially noted. In addition, as the table shows, the T_g values for nanocomposites may be lower than that of the starting polymer. This effect is not considered in terms of the model based on the immobilized-polymer-layer formation.

The formation of a mixed polymer–filler network whose nodes are nanoparticles with surface-adsorbed macromolecules was assumed in [59, 60]. In its essence, this assumption is analogous to the above-mentioned concept contemplating the formation of a "rigid amorphous phase."

What do the above-mentioned approaches have in common? In each of them, the polymer layer near the nanoparticle surface has an effect on the properties of the composite as a whole. In addition, its contribution to the characteristics of a future material is associated with the fact that the volume fraction of the polymer influenced by the surfaces of nanoparticles less than 10 nm in size exceeds the volume fraction of the filler [61]. It is obvious that such parameters as the chemical structure of the nanoparticle surface and the physical, hydrogen, or chemical bonding should predetermine the degree of difficulty in the segmental mobility of macromolecules on the nanoparticle surface or near it [24]. As a consequence, the pretreatment of particles, for example, with finishing agents, can change the degree of interaction between the polymer and the filler. For example, the study of nanocomposites based on natural rubber and nano-SiO$_2$ showed that the chemical structures of finishing agents affect T_g by shifting it in favor of the higher-temperature range [62]. In [44], the reinforcing effect of nanoparticles was found to depend on the length of alkyl groups in the surface modifier of silica particles.

With consideration for the fact that the analyzed systems were obtained via mixing of a polymer solution with a nanoparticle suspension, the quality of the used solvent can serve as an additional factor that changes the properties of an immobilized polymer layer. This assumption was made in [37], whose authors noted that, upon dissolution of PMMA in a more polar solvent (a benzene–acetonitrile mixture) followed by adsorption of the polymer from this solution onto the SiO$_2$ nanoparticle surface, the T_g value of the adsorbed polymer layer is higher than that in the case when a less polar solvent, namely, toluene, is used for the preparation of such samples. This experimental result was attributed to varying density–looseness of polymer coils in a solution, which defines the number of contacts between the polymer chain and the nanoparticle surface.

The quality of a solvent (toluene, 2-butanone, or dimethylacetamide) used for the preparation of PS–silica mixtures [26–31] can be estimated with the use of Hansen solubility parameter χ_H. For calculation of this parameter, we use the Chen equation [63]:

$$\chi_H = \frac{V_L}{RT}\left((\delta_{d,L} - \delta_{d,P})^2 + (\delta_{p,L} - \delta_{p,P})^2\right), \qquad (2)$$

where $\delta_{d,L}$, $\delta_{p,L}$, $\delta_{d,P}$, and $\delta_{p,P}$ are the solubility parameters of a liquid and polymer, respectively; V_L is the molar volume of a liquid; R is the gas constant; and T is temperature. The $\delta_{d,L}$, $\delta_{p,L}$, $\delta_{d,P}$, and $\delta_{p,P}$ values required for calculation [64], as well as the χ_H values, are given below.

Parameter	δ_d	δ_p	V_L, g/cm^3	χ_H
PS	9.64	0.42	–	–
Toluene	8.82	0.7	106.28	0.032
2-Butanone	7.77	4.4	89.59	0.699
Dimethylacetamide	8.2	5.6	93.02	1.086

The χ_H values increase in the order toluene < 2-butanone < dimethylacetamide, which suggests a deterioration in the solvent quality [63]. Following the assumption made in [37], one may expect that the T_g values for the PS-based nanocomposites obtained with the use of dimethylacetamide as the solvent will be lower than those during the application of toluene. As is seen from the table data, the ΔT_g is {+5}–{(–4) or (+2)}–{+6}, respectively, in the toluene–2-butanone–dimethylacetamide series. There is a discrepancy between the experimental and predicted data.

Thus, with the use of one method for the preparation of nanocomposites based on the same polymer, it is possible to observe different effects: increases, constancy, and decreases in the glass-transition temperatures of polymer–nanoparticles mixtures. Note especially that we intentionally did not consider such factor as the effect of nanoparticle size. In the above-cited references, silica particles had diameters in the range 5–30 nm.

The properties of composites obtained from the mixture of a polymer solution and a nanoparticle suspension depend not only on the mixture composition but also on the preparation conditions of films, in particular, on their formation mode and drying condi-

(a)   (b)
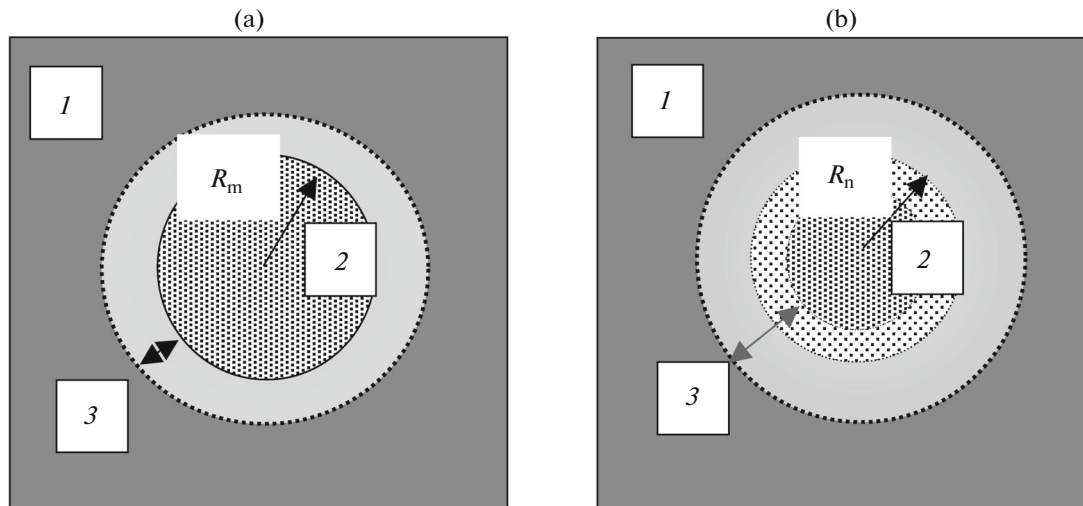
Fig. 1. Formation of the surface layer near a (a) microparticle and (b) nanoparticle: (*1*) matrix polymer, (*2*) filler particles with radius R_m or R_n, and (*3*) surface layer.

tions. In [35], the variation in drying conditions was shown for the example of PS to change the size of aggregates and the modality of the aggregate-size distribution. As a result, T_g for the same-composition system can be higher, remain the same, or be lower than that of the starting polymer. The "disappearing effect" of nanoparticles was noted also by the authors of [65]. They found that annealing the PMMA-based samples and, consequently, release of strains in the film obtained from a solution results in the fact that there is no increase in glass-transition temperature that was observed before annealing. For sure, the plurality and uncertainty of causes influencing the properties of a future material overcomplicate the determination of general regularities in the behavior of polymer–nanoparticles systems and the possibilities for prediction of their characteristics.

Note that solution mixing with the assistance of additional dispersion techniques, as well as preliminary modification of the nanoparticle surface, do not prevent nanoparticle aggregation [24, 25]. Nevertheless, the conditions previously established by P.A. Rehbinder and E.D. Shchukin for the preparation of thermodynamically stable lyophilic systems with particles 1 to 100 nm in size provide a positive attitude for solving this problem. It was shown that the self-dispersion of nanoparticles requires a decrease in the surface tension at the disperse phase/dispersion medium interface to 10^{-2} mJ/m^2 or less [23].

In contrast to the solution method, the method of mixing a polymer melt with nanoparticles, for example, with the use of an extrusion apparatus of a different modification, depends to a lesser degree on the environmental conditions of the experiment [66–70]. Table 1 gives the glass-transition temperatures of systems based on various polymers [71–78]. Either

increases or constancy in the T_g values of composites relative to the glass-transition temperature of the matrix is observed in this case as well. The comparison between the sizes of nanoparticle aggregates forming in the polymer bulk suggests that, during mixing of nanoparticles with a polymer melt, the resulting aggregates are larger than those formed during use of the solution method. Preliminary finishing of the filler surface favors a decrease in the sizes of aggregates that form during mixing.

To explain the effect of nanoparticles on concentration change in the glass-transition temperatures of composites obtained via mixing a polymer melt with a filler, researchers resort to the above-described approaches: either for the effect of poor wetting of the nanoparticle surface with a polymer melt (if T_g of the system remains the same after the addition of silica particles) or for the effect of polymer immobilization on the filler surface (if T_g of the nanocomposite exceeds that of the matrix polymer). The availability of a "convenient approach" creates a situation that does not make the nature of a polymer nanocomposite clearer. This circumstance necessitates performing a number of studies without a clear understanding of what the benefit from the application of nanoparticles is, what kind of properties the nanocomposite will have, where it can be applied, and under which conditions it can be used.

It has been noted above that, after the transition from micro- to nanosized particles, the total surface area of the filler increases significantly and, consequently, the contribution of the properties of the particle-adjacent polymer layer to the overall properties of the composite increases. With a general understanding of how the surface layer influences the characteristics of a material, the conditions of its formation are consid-

ered predominantly from the polymer perspective, i.e., the change in the segmental mobility on or near the surface. The function of the nanoparticle external layer is limited by the function of the "adsorbent" [24]. This approach is valid in the case of composites with micro-sized particles. However, after transitioning to nanoparticles whose size is comparable with the radius of gyration of polymer chain, the morphology and the chemical composition of the external layer of nanoparticle itself, the mobility of its terminal groups, and the compatibility between nanoparticles and polymer can affect the properties of the nearest polymer layer and predetermine the characteristics of the entire nanocomposite. In other words, the nanocomposite surface layer should be regarded most likely as a hybrid structure including both the polymer in proximity to a nanoparticle and the surface layer of the nanoparticle itself (Fig. 1).

The fact that the morphology of the nanoparticle external layer influences the increment in (or its absence from) the glass-transition temperature of the nanoparticle surface-adsorbed polymer was established in [79, 80]. Note that the surfaces of nanosized silica particles used in [80] were not pretreated with finishing agents, but were changed through variation in the preannealing conditions of starting fillers. In [73], it was assumed that the function of the finishing layer is not limited by the increase in the wettability of the nanofiller surface with a polymer or by the change in the number of "adsorption" sites on the particle surface. The finishing layer itself can act as the plasticizer of the nearest polymer layer, a phenomenon that results in a decrease in T_g of the entire composition.

The effect of the nanoparticle external layer on the properties of a composite are better demonstrated by the results from the study of systems containing core–shell particles as the reinforcing agent. The synthesis, properties, and application of such nanostructures are considered in reviews [81, 82]. Molecular silica sols represented by a novel silica form soluble in organic solvents can fit into this class [83]. The main methods for the synthesis of these compounds and their properties are described in [83–87]. The inorganic core of silica sols obtained from hyperbranched polyethoxysiloxane acts as the filler, and the organic shell formed during the synthesis of nanoparticles and covalently bound to the particle inorganic core includes −Si−O−Si−R fragments. Here, R is an organic radical, in particular, [dimethyl(2-phenylethyl)]silyl in the case of a PS matrix polymer. In [88–90], the organic surface layers of nanoparticles 2 nm in size were shown to be, in fact, a compatibilizer of the polymer–nanoparticle system and act as a peculiar "plasticizer" of the matrix polymer. With an increase in the concentration of hybrid nanoparticles in the material, the fraction of the "plasticizer" in the polymer likewise increases. As a consequence, the glass-transition temperatures of polymer–silica sol mixtures decrease monotonically with an increase in the nanoparticle content. The rate

of decrease in T_g of the composition depends on the chemical structure of the nanoparticle external layer, more specifically, the type of external organic groups. It was shown in [89] that, as far as the thermodynamic compatibility between the nanoparticle external groups and the matrix polymer deteriorates, the performance of its external layer as a "plasticizer" decreases.

The contribution of the plasticizing effect of the hybrid-particle surface layer to the properties of a composite depends on the particle size and decreases with an increase in the diameter of the particle inorganic core. In [91, 92], an increase in the core size of an organic−inorganic nanoparticle was found to result in qualitative changes in T_g of the materials. The sign of the shift in this parameter changes from negative to positive in quite a narrow range of the inclusion diameters. With the use of the surface-layer model of a polymer nanocomposite shown in Fig. 1, a novel theoretical approach was developed in [91, 92] to describe the concentration change in T_g of composites with allowance for the configurational entropy of hybrid nanoparticles. It was shown that change in the glass-transition temperatures of composites containing nanosized core−shell particles is mainly caused by the following conditions:

(i) increases in the degrees of freedom and the entropy of system due to the presence of organic-layer hybrid nanoparticles on their surfaces, a situation that favors decreased glass-transition temperatures of composites;

(ii) decreases in the entropy of system disorder and in the number of configuration states of macromolecules in the presence of nanoinclusions, a situation that results in an increased glass-transition temperature of the composition.

The competition between two main factors ultimately defines the increases or decreases in the glass-transition temperatures of materials during an increase in the content of hybrid nanoparticles. The equation describing the glass-transition temperatures of these systems has been obtained [91, 92]:

$$\ln\left(\frac{T_{gc}}{T_{PS}}\right) = \frac{R}{M_p \Delta C_p (1-\varphi)} \left\{ \frac{\varphi}{N_p} \ln \varphi + \frac{1-\varphi}{N} \ln(1-\varphi) \right.$$
$$+ \varphi \ln\left(\frac{Z-1}{e}\right) \tanh^2(R_{cor}/R_K) - \frac{k\varphi}{N} \ln 2$$
$$+ kP\left(\frac{R_p}{R_0}\right) \frac{4\varphi - 3\varphi^2}{1-\varphi} \frac{\varphi}{N_p} \qquad (3)$$
$$- \frac{\varphi}{N_p} \ln(8\pi^2) - 3\frac{\varphi}{N_p} \ln(R_p/R_0)$$
$$\left. - \frac{4}{3} \frac{\varphi}{N_p} \pi \left(\frac{R_p^3 - R_{cor}^3}{R_0^3}\right) \ln v \right\}.$$

Here, $N_{\mathrm{p}} = \dfrac{4\pi R_{\mathrm{pc}}^{3}}{3R_{0}^{3}}$, R is the gas constant, M_{p} is the molar mass of a monomer unit, $\Delta C_{\mathrm{p}}^{(\mathrm{c})}$ (J/(g K)) is the change in the heat capacity of a polymer at the glass transition, R_{K} is the Kuhn segment length of the polymer matrix, R_{pc} is the radius of a nanoparticle, R_{p} is the radius of a particle core, R_{0} is the size of the unit cell, N is the degree of polymerization, $\varphi/N_{\mathrm{p}} = n_{\mathrm{p}}/V$ is the number of particles per unit volume, N_{p} is the number of unit cells corresponding to particles, n_{p} is the number of particles in the system, V is its volume, ν is the orientation number of organic layer units, Z is the coordination number, and φ is the volume fraction of particles.

The proposed approach to describe T_{g} values of the composites with organic–inorganic nanosized particles was tested for the example of such systems as polystyrene with a molecular silica sol having various particle sizes [91, 92] and polystyrene with first, third, and sixth-generation dendrimers [93]. A satisfactory fit between the experimental and theoretical dependences was observed.

The data confirm the above-stated assumption of the "surface layer" composition of nanocomposites (Fig. 1). In our opinion, understanding the morphology and the role of this "layer" and its effect on a material's characteristics provide a key insight into the nature of nanocomposites.

No less an important factor that can influence the properties of a polymer with a nanosized filler is the internal structure of the nanoparticle core, which has an effect on the polymer rigidity and modulus of elasticity. While the moduli of elasticity of composites with microsized inorganic particles are a priori higher than that of the matrix, the situation in nanocomposites is not so unambiguous. According to the data from [88], the modulus of elasticity of a nanocomposite depends on the rigidity of the hybrid nanoparticle core, which is not governed by the numerical value of the elastic modulus, but is based on the molecular concepts of mobility of core-forming chemical bonds. If the particle core can undergo practically no change in shape and is distorted owing to a low mobility of core-forming chemical bonds, its modulus of elasticity is higher and, as a consequence, the modulus of elasticity of the entire composite is higher.

Thus, consideration of the nanocomposite surface layer as a shell including both a polymer and an external layer of nanosized filler, as well as a conditional division between the functions of the external layer and the nanoparticle core, has made it possible to determine in a first approximation which characteristics of the matrix and filler have an effect on the properties of a nanocomposite, in particular, on its glass-transition point and modulus of elasticity. It is obvious that the data are insufficient for the disclosure of general regularities and that only an extension of these approaches to polymer systems of various chemical natures and an extension of the model systems with a core–shell structure can make it possible to control the properties of polymer nanocomposites and to obtain materials with tailor-made characteristics.

REFERENCES

1. S. C. Tjong, Mater. Sci. Eng., R **53**, 73 (2006).
2. *Polymer Nanocomposites,* Ed. by Y.-W. Mai and Z.-Z. Yu (Woodhead Publ. Limited, New York, 2006).
3. A. V. Richard and F. John, Chem. Mater., No. 19, 2736 (2007).
4. B. A. Rozenberg and R. Tenne, Prog. Polym. Sci. **33**, 40 (2008).
5. H. Zou, S. Wu, and J. Shen, Chem. Rev. **108**, 3893 (2008).
6. L. Ruiz-Perez, G. J. Royston, J. P. A. Fairclough, and A. J. Ryan, Polymer **49**, 4475 (2008).
7. J. Njuguna, K. Pielichowski, and S. Desai, Polym. Adv. Technol. **19**, 947 (2008).
8. J. Moczo and B. Pukanszky, J. Ind. Eng. Chem. **14**, 535 (2008).
9. M. Maiti, M. Bhattacharya, and A. K. Bhowmick, Rubber Chem. Technol. **81** (3), 384 (2008).
10. D. R. Paul and L. M. Robeson, Polymer **49**, 3187 (2008).
11. J. Jancar, J. F. Douglas, F. W. Starrf, S. K. Kumar, P. Cassagnau, A. J. Lesser, S. S. Sternstein, and M. J. Buehler, Polymer **51**, 3321 (2010).
12. Y. X. Gan, Micron **43**, 782 (2012).
13. V. A. Gerasin, E. M. Antipov, V. V. Karbushev, V. G. Kulichikhin, G. P. Karpacheva, R. V. Talroze, and Ya. V. Kudryavtsev, Russ. Chem. Rev. **82** (4), 303 (2013).
14. L. Peponi, D. Puglia, L. Torrea, L. Valentini, and J. M. Kenny, Mater. Sci. Eng., R **85**, 1 (2014).
15. A. M. Diez-Pascual, M. A. Gomez-Fatou, F. Ania, and A. Flores, Prog. Mater. Sci **67**, 1 (2015).
16. D. W. Schaefer and R. S. Justice, Macromolecules **40** (24), 8502 (2007).
17. Ph. Cassagnau, Polymer **49**, 2183 (2008).
18. *Functional Fillers for Plastics,* Ed. by M. Xanthos (Wiley-VCH, Weinheim, 2005).
19. A. D. Pomogailo, Russ. Chem. Rev. **69** (1), 53 (2000).
20. V. Bounor-Lgare and Ph. Cassagnau, Prog. Polym. Sci. **39**, 1473 (2014).
21. T. Ogoshi and Y. Chujo, Compos. Interfaces **11** (8–9), 539 (2005).
22. G. Kickelbick, Prog. Polym. Sci. **28**, 83 (2003).
23. B. D. Summ and N. I. Ivanova, Russ. Chem. Rev. **69** (11), 911 (2000).
24. S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, and R. Kumar, Prog. Polym. Sci. **38**, 1232 (2013).
25. M. Tanahashi, M. Hirose, J.-C. Lee, and K. Takeda, Polym. Adv. Technol. **17**, 981 (2006).
26. M. Mizuno, K. Nakamura, T. Konishi, and K. Fukao, J. Non-Cryst. Solids **357**, 594 (2011).

27. A. Bansal, H. Yang, C. Li, K. Cho, B. C. Benicewich, S. K. Kumar, and L. S. Schadler, Nat. Mater. **4**, 693 (2005).

28. P. Rittigstein, R. D. Priestley, L. J. Broadbelt, and J. M. Torkelson, Nat. Mater. **6**, 278 (2007).

29. N. Jouault, P. Vallat, F. Dalmas, S. Said, J. Jestin, and F. Boue, Macromolecules **42**, 2031 (2009).

30. M. Mortezaei, G. Farzi, M. R. Kalaee, and M. Zabihpoor, J. Appl. Polym. Sci. **119**, 2039 (2011).

31. J. S. Meth, S. G. Zane, C. Chi, J. D. Londono, B. A. Wood, P. Cotts, M. Keating, W. Guise, and S. Weigand, Macromolecules **44** (20), 8301 (2011).

32. O. Bera, B. Pilic, J. Pavlicevic, M. Jovicic, B. Hollo, K. M. Szecsenyi, and M. Spirkova, Thermochim. Acta **515**, 1 (2011).

33. J. Moll and S. K. Kumar, Macromolecules **45**, 1131 (2012).

34. S.-L. Huang, W.-K. Chin, and W. P. Yang, Polymer **46** (6), 1865 (2005).

35. S. Sen, Y. Xie, A. Bansal, H. Yang, K. Cho, L. S. Schadler, and S. K. Kumar, Eur. Phys. J.: Spec. Top. **141**, 161 (2007).

36. L. S. Schanler, S. K. Kumar, B. C. Benicewicz, S. L. Lewis, and S. E. Harton, MRS Bull. **32**, 335 (2007).

37. C. E. Porter and F. D. Blum, Macromolecules **33**, 7016 (2000).

38. K. Parker, R. T. Schneider, R. W. Siegel, R. Ozisik, J. C. Cabanelas, B. Serrano, C. Antonelli, and J. Dselga, Polymer **51**, 4891 (2010).

39. J. A. Forrest and J. Mattisson, Phys.Rev. E **61**, R53 (2000).

40. K. J. Lee, D. K. Lee, Y. W. Kim, W.-S. Choe, and J. H. Kim, J. Polym. Sci., Part B: Polym. Phys. **45**, 2232 (2007).

41. Z. Pu, H. Tang, X. Huang, J. Yang, Y. Zhan, R. Zhao, and X. Liu, Colloids Surf., A **415**, 125 (2012).

42. A. S. Sarvestani and E. Jabbari, Polym. Compos. **29**, 326 (2008).

43. S. E. Harton, S. K. Kumar, H. Yang, T. Koga, K. Hicks, H. Lee, J. Mijovic, M. Liu, R. S. Vallery, and D. W. Gigley, Macromolecules **43**, 3415 (2010).

44. S. S. Stenstein and A.-J. Zhu, Macromolecules **35**, 7262 (2002).

45. P. Mele, S. Marceau, D. Brown, Y. de Puydt, and N. D. Alberola, Polymer **43**, 5577 (2002).

46. M. Mortezaei, G. Farzi, M. R. Kalaee, and M. Zabihpoor, J. Appl. Polym. Sci. **119**, 2039 (2011).

47. G. Filippone, G. Romeo, and D. Acierno, Langmuir **26** (4), 2714 (2010).

48. J. Berriot, H. Montes, F. Lequeux, D. Long, and P. Sotta, Macromolecules **35**, 9756 (2002).

49. M. I. Aranguren, E. Mora, J. V. DeGroot, and C. W. Macosko, J. Rheol. **36**, 1165 (1992).

50. N. Jouault, P. Vallat, F. Dalmas, S. R. Said, J. Jestin, and F. Boue, Macromolecules **42**, 2031 (2009).

51. G. Allegra, G. Raos, and M. Vacatello, Prog. Polym. Sci. **33**, 683 (2008).

52. L. M. Hall, A. Jayaraman, and K. S. Schweizer, Curr. Opin. Solid State Mater. Sci. **14**, 38 (2010).

53. J. S. Meth and S. R. Lustig, Polymer **51**, 4259 (2010).

54. V. Arrighi, I. J. McEwen, H. Qian, and M. B. Serrano Prieto, Polymer **44**, 6259 (2003).

55. D. Fragiadakis and P. Pissis, J. Non-Cryst. Solids **353**, 4344 (2007).

56. V. Bershtein, V. Gun'ko, L. Egorova, N. Guzenko, E. Pakhlov, E. Ryzhov, and V. Zarko, Polymer **50**, 860 (2009).

57. M. De Sarkar and P. Deb, Adv. Polym. Technol. **27** (3), 152 (2008).

58. R. B. Bogoslovov, C. M. Roland, A. R. Ellis, A. M. Randall, and C. G. Robertson, Macromolecules **41**, 1289 (2008).

59. G. A. Huber and T. Vilgi, Macromolecules **35**, 9204 (2002).

60. M. Bailly, M. Kontopoulou, and K. El Mabrouk, Polymer **51** (23), 5506 (2010).

61. A. Navrotsky, J. Chem. Thermodyn. **39**, 2 (2007).

62. T. Theppradit, P. Prasassarakich, and S. Poompradub, Mater. Chem. Phys. **148**, 940 (2014).

63. S. Chen, J. Appl. Polym. Sci. **15**, 1247 (1971).

64. A. E. Nesterov, *Handbook on Physical Chemistry of Polymers* (Naukova Dumka, Kiev, 1984), Vol. 1.

65. C. Hub, S. E. Harton, M. A. Hunt, R. Fink, and H. Ade, J. Polym. Sci., Part B: Polym. Phys. **45**, 2270 (2007).

66. M. Tanahashi, Materials **3**, 1593 (2010).

67. F. Yang and G. L. Nelson, Polym. Adv. Technol. **17**, 320 (2006).

68. M. Tanahashi, M. Hirose, J.-C. Lee, and K. Takeda, Polym. Adv. Technol. **17**, 981 (2006).

69. X. M. Sang, X. J. Yang, Z. D. Cui, S. L. Zhu, and J. Sheng, J. Macromol. Sci., Part B: Phys. **44**, 237 (2005).

70. A. Christmann, P. Ienny, J. C. Quantin, A. S. Caro-Bretelle, and J. M. Lopez-Cuesta, Polymer **52**, 4033 (2011).

71. E. Kontou and G. Anthoulis, J. Appl. Polym. Sci. **105**, 1723 (2007).

72. J. L. H. Chau and S. L.-C. Hsu, Y.-M. Chen, C.-C. Yang, and P. C. F. Hsu, Adv. Powder Technol. **21**, 341 (2010).

73. T. E. Motaung, M. L. Saladino, A. S. Luyt, and D. F. Chillura Martino, Compos. Sci. Technol. **73**, 34 (2012).

74. M. Biswal, S. Mohanty, S. K. Nayak, and P. S. Kumar, Polym. Eng. Sci. **53**, 1287 (2013).

75. Y. Feng, B. Wang, F. Wang, G. Zheng, K. Dai, C. Liu, J. Chen, and C. Shen, J. Reinf. Plast. Compos. **33**, 911 (2014)

76. M. L. Saladino, T. E. Motaung, A. S. Luyt, A. Spinella, G. Nasillo, and E. Caponetti, Polym. Degrad. Stab. **97**, 452 (2012).

77. D. Olmos, S. G. Prolong, and G. Gonzalez-Benito, Composites, Part B **61**, 307 (2014).

78. X. Chen, J. Gug, and M. J. Sobkowicz, Compos. Sci. Technol **95**, 8 (2014).

79. P. Klonos, I. Ya. Sulym, K. Kyriakos, I. Vangelidis, S. Zidropoulos, D. Sternik, M. V. Borysenko, A. Kyritsis, A. Deryło-Marczewska, V. M. Gun'ko, and P. Pissis, Polymer **68**, 158 (2015).

80. R. R. Madathingal and S. L. Wunder, Langmuir **26** (7), 5077 (2010).

81. J. Z. Ma, Y. H. Liu, Y. Bao, J.-L. Liu, and J. Zhang, Adv. Colloid Interface Sci. **197−198**, 118 (2013).

82. R. G. Chaudhuri and S. Paria, Chem. Rev. **112**, 2373 (2012).

83. V. V. Kazakova, A. N. Ozerin, and A. M. Muzafarov, in *Silicones and Silicone-Modified Materials,* Ed. by S. J. Clarson, J. J. Fitzgerald, and M. J. Owen (Am. Chem. Soc, Washington, DC, 2000).

84. N. V. Voronina, I. B. Meshkov, V. D. Myakushev, T. V. Laptinskaya, V. S. Papkov, M. I. Buzin, M. N. Il'ina, A. N. Ozerin, and A. M. Muzafarov, J. Polym. Sci., Part A: Polym. Chem. **48**, 4310 (2010).

85. N. V. Voronina, I. B. Meshkov, V. D. Myakushev, N. V. Demchenko, T. V. Laptinskaya, and A. M. Muzafarov, Nanotechnol. Russ. **3** (5), 321 (2008).

86. A. M. Muzafarov, N. G. Vasilenko, E. A. Tatarinova, G. M. Ignat'eva, V. M. Vyakushev, M. A. Obrezkova, I. V. Meshkov, N. V. Voronina, and O. V. Novozhilov, Polym. Sci., Ser. C **53** (1), 48 (2011).

87. V. V. Kazakova, A. S. Zhiltsov, O. B. Gorbatsevich, I. B. Meshkov, M. V. Pletneva, N. B. Demchenko, G. V. Cherkaev, and A. M. Muzafarov, J. Inorg. Organomet. Polym. **22**, 564 (2012).

88. O. A. Serenko, M. V. Mironova, N. A. Novozhilova, P. V. Strashnov, E. V. Getmanova, A. A. Askadskii, V. G. Shevchenko, V. G. Kulichikhin, and A. M. Muzafarov, Mater. Chem. Phys. **156**, 16 (2015).

89. A. Zhiltsov, O. Gritsenko, V. Kazakova, O. Gorbatsevitch, N. Bessonova, A. Askadskii, O. Serenko, and A. Muzafarov, J. Appl. Polym. Sci. (2015) (in press). doi 10.1002/app.41894

90. E. A. Karpukhina, S. O. Il'in, V. V. Makarova, I. B. Meshkov, and V. G. Kulichikhin, Polym. Sci., Ser. A **56** (6), 798 (2014).

91. V. I. Roldughin, O. A. Serenko, E. V. Getmanova, N. A. Novozhilova, G. G. Nikifirova, M. I. Buzin, S. N. Chvalun, A. N. Ozerin, and A. M. Muzafarov, Polym. Comp. (in press). doi 10.1002/pc.23376

92. V. I. Roldugin, O. A. Serenko, E. V. Getmanova, N. A. Karmishina, S. N. Chvalun, and A. M. Muzafarov, Dokl. Phys. Chem. **449**, 83(2013).

93. N. A. Novozhilova, O. A. Serenko, V. I. Roldugin, A. A. Askadskii, and A. M. Muzafarov, Silicon **7**, 155 (2015).

Translated by K. Utegenov