Assessing the glass transition temperature of nanocomposites based on copolymers of styrene butadiene rubber, polyisoprene, and polybutadiene

T.A. Matseevich,1 A.A. Askadskii,1,2 M.N. Popova,1 O.V. Kovriga,2 and E.S. Afanas’ev2

1Moscow State University of Civil Engineering, Moscow
2A.N. Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences, Moscow

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SUMMARY

A theoretical analysis was made of the effect of nanoparticles on the glass transition temperature of polymer nanocomposites. Account was taken of the effect of the chemical structure of the polymer matrix and the concentration, size, and shape of the nanoparticles. Experimental checking was done for nanocomposites based on copolymers of styrene butadiene rubber, polyisoprene, and polybutadiene.

Assessment of the effect of nanoparticles on the glass transition temperature in nanocomposites is a matter of constant interest. This is particularly important when the surface of the nanoparticles is modified with polar groups, which can both chemically interact with the polymer matrix and enter into intermolecular interaction. The compatibility (‘solubility’) of these groups with the material of the polymer matrix is also important. A thermodynamic approach to the given problem is laid out in Roldugin et al. [1]. As a result, the dependences of the difference in the glass transition temperatures of the initial polymer and of nanocomposites based on it, which have a positive or negative slope, were obtained.

In this work, an analysis is made of the possibility of assessing the glass transition temperature of nanocomposites based on approaches proposed elsewhere [2–5]. In examining the effect of solid nanoparticles introduced into the polymer matrix on the glass transition temperature of polymer nanocomposites, we will take the following factors into account: (1) the chemical structure of the polymer; (2) the chemical structure of the nanoparticles and their surface in the case of modification; (3) the concentration of nanoparticles and their shape (spherical, lamellar, cylindrical); (4) the concentration (number) of functional groups on the surface of the nanoparticle; (5) the energy of intermolecular interaction between polymer and nanoparticle; (6) the possibility of chemical interaction between polymer and nanoparticle surface.

The principle of calculating the glass transition temperature of linear and crosslinked polymers, and also their blends, is set out in earlier monographs [2–5]. If the nanoparticles contain a certain number of polar groups on their surface owing to their modification, additional intermolecular interaction occurs. This is taken into account by introducing an additional term into the equation [2–5] for calculating the glass transition temperature of the polymer $T_g$. In the case of a polymer network, the resulting equation looks as follows:

$$T_g = \frac{\left(\sum_i \Delta V_i\right)_{0}}{\sum_i a_i \Delta V_i + \sum_j \Delta V_j} + \left(\sum_i K_i \Delta V_i\right)_{braid} - b_{\beta} \beta \beta$$

where $\left(\sum_i \Delta V_i\right)_{0}$ is the van der Waals volume of the recurring fragment of the network, $\left(\sum_i a_i \Delta V_i + \sum_j \Delta V_j\right)$ is the set of atomic constants for linear chains entering into the recurring fragment of the network, $\left(\sum_i K_i \Delta V_i\right)_{braid}$ is the...
set of atomic constants for a crosslinked point of the network, $\beta$ is the number of polar groups localised on the surface of the nanoparticles in terms of the recurring fragment of the network, $b_{d,h}$ is the constant $b_j$ taking into account the effect of the polar groups possessing dipole–dipole interaction ($b_d$) or hydrogen bonds ($b_h$).

The quantity $\beta$ is determined in the following way. In the case of spherical nanoparticles, their number $n_{np}$ per gram of nanocomposite is equal to:

$$n_{np} = \frac{c_{np}}{g_{np}} = \frac{3c_{np}}{\rho_{np} 4\pi R_{np}^3}$$

(2)

where $c_{np}$ is the weight of the nanoparticles in the nanocomposite, $g_{np}$ is the weight of a single nanoparticle, $\rho_{np}$ is the density of a nanoparticle, and $R_{np}$ is the radius of a nanoparticle.

The number of polar groups $N_{pg}$ on the surface of all the nanoparticles in the given system is equal to:

$$N_{pg} = \frac{3n_{pg} \cdot c_{np}}{\rho_{np} 4\pi R_{np}^3}$$

(3)

where $n_{pg}$ is the number of polar groups on the surface of one nanoparticle.

The total number of recurring fragments $N_r$ in the examined system is equal to:

$$N_r = \frac{c_p \cdot M_0}{0.6023 \times 10^{24}}$$

(4)

where $c_p$ is the weight of the polymer, and $M_0$ is the molecular weight of the recurring fragment of the network.

The number of polar groups per recurring fragment of the network is equal to:

$$\beta = \frac{3n_{pg} \cdot c_{np} \cdot M_0}{\rho_{np} 4\pi R_{np}^3 \cdot c_p \cdot 0.6023 \times 10^{24}}$$

(5)

Substituting formula (5) into equation (1), we obtain:

$$T_g = \frac{\left(\sum_{i} \Delta V_i \right)_0}{\left(\sum_{i} a_i \Delta V_i + \sum_{j} b_j \right)_\text{linear} + \left(\sum_{i} K_i \Delta V_i \right)_\text{crosslink} - b_{dh} \frac{3n_{pg} \cdot c_{np} \cdot M_0}{\rho_{np} 4\pi R_{np}^3 \cdot c_p \cdot 0.6023 \times 10^{24}}}$$

(6)

If on the surface of the nanoparticles there are groups leading to the formation of hydrogen bonds, then $b_{dh} = 140 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1}$ [2]. Given that on the surface of the SiO$_3$ nanoparticles there are OH groups, we will use this quantity. Furthermore, as the radius of the nanoparticle is expressed in Å, the final expression for calculating the glass transition temperature of the nanocomposites takes the following form:

$$T_g = \frac{\left(\sum_{i} \Delta V_i \right)_0}{\left(\sum_{i} a_i \Delta V_i + \sum_{j} b_j \right)_\text{linear} + \left(\sum_{i} K_i \Delta V_i \right)_\text{crosslink} - 140 \times 10^{-3} \frac{3n_{pg} \cdot c_{np} \cdot M_0}{\rho_{np} 4\pi R_{np}^3 \cdot c_p \cdot 0.6023}}$$

(7)

Let us determine the constants of expression (7) for specific networks. The structure of the rubbers and their glass transition temperatures are given below:

![Structure of the rubber](image)

$T_g \approx -25^\circ \text{C}$, styrene butadiene rubber
\[ T_g \sim -100^\circ C, \text{ butadiene rubber} \]

\[ T_g \sim -70^\circ C, \text{ natural rubber} \]

We will carry out calculations using the Kaskad computer program (Institute of Heteroorganic Compounds, Russian Academy of Sciences). For styrene butadiene rubber, the composition of which is given above, the calculated glass transition temperature is 247 K; for butadiene rubber of 1,4-structure, \( T_g = 171 \) K; for natural rubber, \( T_g = 203 \) K. These data are in good agreement with experimental data [6].

Initially we will conduct an analysis in general form, and then we will analyse data obtained in Arrighi et al. [6]. If for one crosslinked point of the network there are \( n \) recurring units of linear chains, expression (7) is written in the form:

\[
T_g = \frac{n \left( \sum \Delta V_i \right)_{\text{linear}} + \left( \sum \Delta V_i \right)_{\text{crosslink}}}{n \left( \sum \Delta V_i \right)_{\text{linear}} + \left( \sum \Delta V_i \right)_{\text{crosslink}}} + \frac{140 \times 10^{-3} \frac{3n \rho c M_0}{4\pi R^3}}{c_0 0.6023} \tag{8}
\]

where \( \sum \Delta V_i \) is the van der Waals volume of a crosslinked point, and \( \sum \Delta V_i \) is the van der Waals volume of the recurring unit of the linear chains connecting the crosslinked points.

For styrene butadiene rubber, the structure of which is shown above, \( \sum \Delta V_i = 75.6 \ \text{Å}^3 \), \( T_g = 247 \) K, and \( \sum \Delta V_i = 56.2 \ \text{Å}^3 \).

For a crosslinked point, \( T_g = 717 \) K. According to a definition given elsewhere [2–5], a crosslinked point can be shown as follows:

\[
\begin{array}{c}
\text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_2 \\
\end{array}
\]

As the glass transition temperature of the linear polymer is determined from the equation [2–5]:

\[
T_g = \frac{\left( \sum \Delta V_i \right)_{\text{linear}}}{\left( \sum a_i \Delta V_i + \sum b_j \right)_{\text{linear}}} \tag{9}
\]

it follows that \( \left( \sum a_i \Delta V_i + \sum b_j \right)_{\text{linear}} = 306 \times 10^{-3} \ \text{Å}^3 K^{-1} \). The magnitude of \( T_g \) for a crosslinked point is determined from the relation [2–5]:

\[
T_g = \frac{\left( \sum \Delta V_i \right)_{\text{crosslink}}}{\left( \sum K_i \Delta V_i \right)_{\text{crosslink}}} \tag{10}
\]
Then \( \left( \sum_{i} K_i \Delta V_i \right)_{\text{crosslink}} = 78.4 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1} \).

The molecular weight of the recurring unit is 66.6. The density of an \( \text{SiO}_2 \) nanoparticle \( \rho_{\text{np}} \) is 2.02 g/cm\(^3\) (calculated using the Kaskad computer program). Substituting all the calculated quantities into relation (8), and taking into account that \( c_p = 1 - c_{\text{np}} \), we have:

\[
T_g = \frac{n75.6 + 56.2}{n0.306 + 0.0784 - 1.83 \frac{n_{pg} c_{np}}{R_{np}^3 (1 - c_{np})}}
\]

Let us analyse the influence of all the parameters on the glass transition temperature. Above all, we will assess the influence of the number of units \( n \) in the linear chain between crosslinked points \( n \). The dependence of the glass transition temperature on \( n \) with a nanoparticle radius \( R_{np} \) of 10 nm and a number of groups on their surface \( n_{pg} \) of 10 000 is shown in Figure 1.

It can be seen that the glass transition temperature decreases rapidly with increase in \( n \) in the range from 1 to 10, and then decreases very little, turning, at large \( n \), into the glass transition temperature of the linear polymer. The nanoparticle concentration has little effect on \( T_g \).

Let us now analyse the dependence of the glass transition temperature on the number of OH groups at \( n = 5 \) for a nanoparticle radius of 4 nm and a different concentration of nanoparticles in the composite (Figure 2).

From Figure 2 it follows that the glass transition temperature increases little with increase in the number of OH groups on the nanoparticle surface.

We will now consider the dependence of \( T_g \) on the nanoparticle concentration at a radius of 4 nm, and with a number of OH groups on the nanoparticle surface \( n_{pg} = 1000 \) (Figure 3).

Finally, we will obtain the dependence of the glass transition temperature on the nanoparticle radius (Figure 4). We will assume that \( n = 5 \) and \( n_{pg} = 1000 \). Using expression (11), we obtain the dependences of \( T_g \) on \( R_{np} \) at different nanoparticle concentrations.

The dependence of \( T_g \) on the nanoparticle radius is pronounced only with small radii; at large radii and a small number of polar OH groups, the glass transition temperature approaches \( T_g \) of the initial polymer.

We will analyse the polymer nanocomposite whose composition and properties are described in Arrighi et al. [6]. The polymer matrix of the nanocomposite consists of 23.5% polystyrene, 10% 1,2-polybutadiene, and 66.5% 1,4-polybutadiene. For such a system, using the Kaskad program, the following values of the parameters were obtained: \( \sum_{i} \Delta V_i \) \( \text{linear} = 74.9 \text{ Å}^3 \), \( T_g = 210 \text{ K} \), and \( M_0 \).
For a crosslinked point, $T_g = 717$ K. Using formulae (9) and (10), we establish that
$$< \sum_i \Delta V_i > \text{crosslink} = 56.2 \text{ Å}^3.$$

For a crosslinked point, $T_g = 717$ K. Using formulae (9) and (10), we establish that
$$< \sum_i a_i \Delta V_i + \sum_j b_j > \text{linear} = 356.7 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1},$$
and
$$< \sum_i k_i \Delta V_i > \text{crosslink} = 78.4 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1}.$$

Substituting these parameters, and also the experimental value $T_g = 238.5$ K, into equation (8), we obtain:
$$T_g = \frac{74.9n + 56.2}{0.3567n + 0.0784} = 238.5$$
(12)

From this expression we find that $n = 3.7$.

The density of an SiO$_2$ nanoparticle $\rho_{np}$ was 2.02 g/cm$^3$ (calculated using the Kaskad program). Substituting all the calculated quantities into relation (11), and taking into account that $c_p = 1 - c_{np}$, we have:
$$T_g = \frac{333.3}{1.3982 - 1.811 \frac{n_{pg} c_{np}}{R_{np}^3 (1 - c_{np})}}$$
(13)

We will determine the nanoparticle radius. In Arrighi [6] it was shown that the specific surface of the nanoparticles amounts to $\sim 160$ m$^2$/g. Simple estimation indicates that the average radius of the nanoparticles with such a surface amounts to 9.3 nm. We will assume, for subsequent calculations, that $R_{np} = 10$ nm. Remember that $R_{np}$ in formula (11) is expressed in Å, and therefore, for calculations, we must use the value $R_{np} = 100$ Å.

The dependence of the glass transition temperature on the weight fraction of the nanoparticles is shown in Figure 5. The glass transition temperature increases negligibly with increase in the nanoparticle concentration; this increase is most appreciable at large values of the number of OH groups on the nanoparticle surface $n_{pg}$. According to Arrighi’s data [6], when SiO$_2$ nanoparticles whose surface has not been treated are introduced, the glass transition temperature hardly changes. This corresponds to a relatively small content of polar OH groups on the nanoparticle surface (1000–3000).

To treat the surface of the SiO$_2$ nanoparticles, use is made of the TESPT product, the chemical structure of which is shown in Scheme 1 [6].

This product, when introduced into the rubber blend, interacts chemically with the OH groups on the nanoparticle surface, and also serves as a curing agent of the rubber. The scheme of such interaction is also shown here. As a result, crosslinked units are formed of the following chemical structure:

![Chemical structure of crosslinked units](image)

The glass transition temperature of a crosslinked point $T_g = 298$ K, the molecular weight of a crosslinked point is 565, and the van der Waals volume is 449 Å$^3$.

![Figure 4](image)

Figure 4. The dependence of the glass transition temperature on the nanoparticle radius. Number of units in fragments between crosslinked points $n = 5$. Number of OH groups on the surface of a single nanoparticle 1000. Nanoparticle concentration in the composite: 1 – 10 wt%; 2 – 20 wt%; 3 – 30 wt%; 4 – 40 wt%; 5 – 50 wt%;

![Figure 5](image)

Figure 5. The dependence of the glass transition temperature on the nanoparticle concentration. Number of OH groups on the surface of a single nanoparticle: 1 – 1000; 2 – 2000; 3 – 3000; 4 – 5000; 5 – 7000; 6 – 10 000
Substituting these quantities into equation (10), we find that 
\[
\sum K_i \Delta V_i = 1507 \times 10^{-3} \text{Å}^3 \text{K}^{-1}
\]

We will now take into account that, when the product TESPT is introduced, some of the ‘normal’ crosslinked points are replaced by the crosslinked points shown above. Taking the parameters of these crosslinked points (see above) into account, we will write:

\[
T_g = \frac{277.1 + (1 - \alpha) \cdot 56.2 + 449 \alpha}{1.3198 + (1 - \alpha) \cdot 0.0784 + 1.507 \alpha} \tag{14}
\]

As the van der Waals volume of this new crosslinked point is considerably higher than the volume of a ‘normal’ crosslinked point, the parameters must be reduced to the volume of a ‘normal’ crosslinked point. For this, we will multiply all the parameters relating to the new crosslinked point by the ratio of van der Waals volumes of these crosslinked points 56.2/449 = 0.125. Then we obtain:

\[
T_g = \frac{277.1 + 56.2}{1.319 + (1 - \alpha) \cdot 0.078 + \alpha \cdot 0.1884} \tag{15}
\]

where \(\alpha\) is the proportion of new crosslinked points that arise during treatment with TESPT.

Calculation by means of relation (15) leads to the following dependence of glass transition temperature on proportion of new crosslinked points (Figure 6).

When the nanoparticles are treated with TESPT, the glass transition temperature decreases slightly, which is confirmed by experiments in Arrighi et al. [6]. The dependence of \(T_g\) on \(\alpha\) can be calculated more accurately if account is taken of the presence of OH groups that are not consumed in the course of the curing reaction. For this, use will be made of relation (13), which will be rewritten in the form:

\[
T_g = \frac{333.3}{1.319 + 0.0784(1 - \alpha) + 0.1884\alpha - 1.811 \frac{n_{\text{OH}}}{R^3(1 - c_{\text{mp}})} \tag{16}}
\]

![Figure 6](image-url)
For $c_{np} = 0.5$ and $R_{np} = 10$ nm (100 Å), the dependences of the glass transition temperature on $\alpha$ with different numbers of OH groups on the surface $n_{pg}$ are shown in Figure 7.

If the glass transition temperature decreases to 234.5 K, the proportion of crosslinked points formed as a result of TESPT treatment is 0.15.

Now let us examine the effect of an agent covering the surface of the nanoparticles, namely triethoxyoctylsilane (OCTEO). This substance chemically interacts only with OH groups on the surface of the SiO$_2$ nanoparticles, as a result of which the following compound is formed:

Each triethoxyoctylsilane molecule reacts with two OH groups on the nanoparticle surface, and therefore the number of hydrogen bonds during each such interaction decreases by 2. The molecular weight of this structure $M^* = 323$. We will take this fact into account by modifying expression (13). To begin with, we will calculate the number of triethoxyoctylsilane molecules on the surface of a single nanoparticle. The total number of introduced triethoxyoctylsilane molecules is equal to $c_{ca} \cdot 0.6023 \cdot 10^{24}/M^*$, where $c_{ca}$ is the number of grams of covering agent triethoxyoctylsilane per gram of nanocomposite. The number of nanoparticles per gram of nanocomposite is equal to $3c_{np}/4\pi R_{np}^3$.

Then, with these relations taken into account, we find that the number of triethoxyoctylsilane molecules $n^*$ chemically bound with the surface of a single nanoparticle is equal to:

$$n^* = \frac{0.6023\rho_{np} 4\pi R_{np}^3 c_{ca}}{M^* 3c_{np}}$$

(17)

When relation (13) is used, we will take into account that one triethoxyoctylsilane molecule excludes two OH groups from hydrogen bonding. Then, relation (13) is transformed into the following formula:

$$T_g = \frac{333.3}{1.3982 - 1.811(0.01 - 0.063c_{ca})}$$

(18)

We will plot the dependence of $T_g$ on the amount of triethoxyoctylsilane introduced per gram of nanocomposite with the following parameters: $M^* = 323$, $c_{np} = 0.5$, $R_{np} = 10$ nm (100 Å), $n_{pg} = 10000$. With such parameters, from formula (18) we obtain the following expression:

$$T_g = \frac{333.3}{1.3982 - 1.811(0.01 - 0.063c_{ca})}$$

(19)

The dependence of $T_g$ on $c_{ca}$ is shown in Figure 8. A small reduction is observed in the glass transition temperature with increase in the concentration of triethoxyoctylsilane introduced. The calculated values of the glass transition temperatures are in satisfactory agreement with the experimental data [6].

Thus, the calculation schemes proposed make it possible to assess the influence of the chemical structure of the polymers (copolymers) and nanoparticles, and also the shape and concentration of the nanoparticles and the possibility of chemical interaction with the
polymer matrix, on the glass transition temperature of the polymer nanocomposites. The calculation schemes are of general nature and can be applied to polymers and nanoparticles of different classes.

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