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Polymeric nanocomposites: account for the effect of size distribution of nanoparticles

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Abstract. The essence of the work lies in the theoretical analysis of the influence of size distribution of nanoparticles in polymer nanocomposites on the glass transition temperature \( T_g \) and coefficient of thermal expansion CTE. Both of these characteristics are important for building materials containing polymers. If the values of these characteristics exceed the allowable value, the material will soften and you should not alter its size.

Methods: used the Poisson distribution applied to the radius of the nanoparticles. The analysis is performed at the expected mean values of 5 and 10 nm. As object of research used in the cured epoxy resin filled with nanoparticles of SiO2. The surface modified nanoparticles grafted polar groups possessing a dipole-dipole interaction and hydrogen bonds. The analysis is based on previously obtained relationships connecting the \( T_g \) and CTE with a set of atomic physical constants. This set depends on the chemical structure of the repeating unit of the polymer or molecular fragment of a polymer network. Among these constants, Van-der-Waals volume and the energy of the dispersion interaction of each atom, as well as energy dipole-dipole interaction or hydrogen bonds to polar groups.

The results of the study: they consist in the fact that the dependencies of \( T_g \) and CTE on the expected mean radius of nanoparticles are obtained. Considered part of the epoxy resin will be cured with usual methylhydrophthalic anhydride and another part of the epoxy resin will be cured with anhydride-modifier. The formulas for quantitative assessment of the values of \( T_g \) and CTE for such copolymer structures are obtained. The greatest increase in \( T_g \) of 430 to 465 K was observed when reducing the radius of the nanoparticles from 8 to 3 nm at the mean expected value of 5 nm. This is true when chemical interaction between the epoxy resin and anhydride-modifier takes place. The magnitude of the CTE increases from 1.95×10^{-4} up to 2.05×10^{-4} by increasing mean radius of nanoparticles from 3 to 7 nm.

Conclusions: The expression for the theoretical estimation of \( T_g \) value of nanocomposites was modified in order to account for the polydispersity of nanoparticles. The theoretical estimation shows that the influence of the size distribution of the silica nanoparticles on the both of \( T_g \) and CTE values of the epoxy/silica nanocomposite can be quite considerable. The most significant effect will be achieved at the conditions, when nanoparticles play the role of multifunctional curing agent.

Keywords: nanoparticles, Poisson distribution, epoxy resin, SiO2, glass transition temperature, coefficient of thermal expansion, Van-der-Waals volume, dipole-dipole interaction, hydrogen bonds.
1. Introduction
The present paper is aimed to get a deep fundamental understanding of the general mechanism of the
effect of distribution of nanoparticles on the glass transition temperature $T_g$ and the coefficient of
thermal expansion (CTE). Both of characteristics are important for polymer materials, because the
glass transition temperature defines the ability to use the material as structural. The coefficient of
thermal expansion is a fundamental characteristic to assess the influence of temperature on change of
the size of the construction.

Currently nanomaterials is receiving increasing attention, but the description of the glass transition
temperature and coefficient of thermal expansion is very limited [1-10]. In [2] investigated styrene-
butadiene rubber containing silica nanofiller. In a series of papers [3-10] investigated the thermal
properties of nanocomposites based on polyimide. The nanotubes from graphene or SiO2 particles
were used. The most interesting experimental data [10] on nanocomposite films based on fluorinated
polyimides, filled with organo-modified montmorillonite concentration of the latter from 1 to 4 wt. %.
Found reduction of the coefficients of thermal expansion and increasing thermal stability.

In all cited works do not address the influence of size distribution of nanoparticles on the glass
transition temperature and coefficient of thermal expansion. Let us conduct theoretical analysis of this
issue.

2. Methods
Let us examine 1 g composite containing epoxy resin, nanoparticles, and modifier of the surface of
nanoparticles. The following notations are introduced: $c_{er}$ is the weight of epoxy resin, $c_{np}$ is the weight
of nanoparticles, $c_m$ is the weight of modifier. So,

$c_{er} + c_{np} + c_m = 1g.$

The number of moles for epoxy resin is equal to

$$\frac{c_{er}}{M_{rf}},$$

where $M_{rf}$ is the molecular mass of the repeating fragment of the cured epoxy resin.

The number of such fragments containing in 1 g of nanocomposite is equal to

$$\frac{c_{er}}{M_{rf}} N_A = c_{er} \cdot 0.6023 \cdot 10^{24}.$$  \hspace{1cm} (2)

The volume of nanoparticle $v_{np}$ is evaluated by formula

$$v_{np} = \frac{4}{3} \pi R_{np}^3,$$

where $R_{np}$ is the radius of nanoparticle.

The weight of nanoparticle $g_{np}$ is

$$g_{np} = \rho_{np} \cdot v_{np} = \rho_{np} \frac{4}{3} \pi R_{np}^3.$$  \hspace{1cm} (4)

The number of nanoparticles $n_{np}$ containing in 1 g of nanocomposite is

$$n_{np} = \frac{c_{np}}{g_{np}} = \frac{3 c_{np}}{\rho_{np} \cdot 4 \pi R_{np}^3}.$$  \hspace{1cm} (5)

The number of moles for modifier introduced for treatment of nanoparticles is equal to

$$\frac{c_m}{M_m},$$

and the number of molecules of modifier is

$$\frac{c_m}{M_m} \cdot N_A = \frac{c_m}{M_m} \cdot 0.6023 \cdot 10^{24}.$$  \hspace{1cm} (7)

The number of modifier molecules per 1 repeating fragment of a cured epoxy resin is calculated by
formula
\[
\frac{c_m - 0.6023 \cdot 10^{24}}{M_m} = \frac{c_{\text{ref}} - 0.6023 \cdot 10^{24}}{M_{\text{ref}}}.
\]

Now let us estimate the area of surface for all the nanoparticles. The area of surface for 1 nanoparticle \(s_{np} \) is \( s_{np} = 4\pi R_{np}^2 \) and the area of surface for all the nanoparticles is

\[
S_{np} = 4\pi R_{np}^2 \cdot \frac{3c_{np}}{\rho_{np} 4\pi R_{np}^3} = \frac{3c_{np}}{\rho_{np} R_{np}}.
\]

Let us denote the Van-der-Waals volume of the molecule of modifier as \( \sum_i \Delta V_i \). So, the actual volume \( v_m \) of the molecule of modifier is

\[
\left( \sum_i \Delta V_i \right)_m = \frac{k}{\pi R_m^3} = \frac{3}{4\pi k} \left( \sum_i \Delta V_i \right)_m.
\]

The area of a molecule of modifier is

\[
s_m = \pi R_m^2 = \pi \left( \frac{3}{4\pi k} \left( \sum_i \Delta V_i \right)_m \right)^{2/3}
\]

The area of all the molecules of modifier is estimated by following formula

\[
S_m = \frac{c_m - 0.6023 \cdot 10^{24}}{M_m} \left( \frac{3}{4\pi k} \left( \sum_i \Delta V_i \right)_m \right)^{2/3}.\]

Now it is necessary to compare the area of all the molecules of modifier forming one monolayer on the surface of nanoparticle with the area of surface for all the nanoparticles. If a monolayer on the surface of nanoparticles is formed, the following relation takes place:

\[
\frac{c_m - 0.6023 \cdot 10^{24}}{M_m} \left( \frac{3}{4\pi k} \left( \sum_i \Delta V_i \right)_m \right)^{2/3} = \frac{3c_{np}}{\rho_{np} R_{np}}.
\]

From this equation we have:
\[
c_m = \frac{3c_{np}M_m}{\rho_{np}R_{np}0.6023\cdot10^{24}\pi} \left[ \frac{3}{4\pi k} \sum_i \Delta V_i \right]^{2/3}.
\]

If \( M_m = 80 \), \( \sum_i \Delta V_i \mid_m = 70 \, \text{Å}^3 \), \( c_{np} = 0.1 \), \( \rho_{np} = 0.74 \, \text{g/cm}^3 \), we obtain:

\[
c_m = 2.029 \cdot 10^3/R_{np}.
\]

Now let us compare the number of modifier molecules in the composite with the number of the repeating fragments of the network (note that \( M_{rf} \) for the epoxy resin cured with methylhydrophthalic anhydride is equal to 589):

\[
c_m \frac{M_{rf}}{c_{er}} = \frac{2.029 \cdot 10^3 \cdot 589}{80 \cdot 0.88R_{np}}.
\]

When a size distribution of the nanoparticles takes place, the problem is complicated. Let us examine the Poisson’s distribution:

\[
f(x) = \frac{\lambda^x \exp(-\lambda)}{x!},
\]

where \( x = 1, 2, 3, \ldots, n \); \( \lambda \) is the expected mean value. For the case mentioned above \( x \) is the value of the radius of nanoparticles (nm); \( \lambda = R_{av, np} \) (mean value of the radius of nanoparticles).

Preliminary we note that

\[
\sum_{i,j} c_{ms}M_{rf} = A \sum_{x=1}^n f(x)c_{ms},
\]

where \( A = \frac{b_d M_{rf}}{M_{er} c_{er}} \).

The glass transition temperature is described by equation [11]

\[
T_g = \frac{\sum_i \Delta V_i}{\sum_i a_i \Delta V_i + \sum_j b_j} + \frac{\sum_i K_i \Delta V_i}{\sum_i K_i \Delta V_i} - 55 \cdot 10^{-3} \frac{C_{ms}M_{rf}}{M_m c_{er}}.
\]

Then the equation (18) transforms to the form:

\[
T_g = \frac{\sum_i \Delta V_i}{\sum_i a_i \Delta V_i + \sum_j b_j} + \frac{\sum_i K_i \Delta V_i}{\sum_i K_i \Delta V_i} - 0.934 \cdot 10^{-8} \sum_{R_{np}} f(R_{np}),
\]

where

\[
f(R_{np}) = \frac{\lambda^{R_{av, np}} \exp(-R_{av, np})}{x!}.
\]

If the hydrogen bonds appear as a result of modification, using equation (18) we obtain:
The results of the study

Now let us examine an influence of the size distribution for nanoparticles on the glass transition temperature when chemical interaction between modifier and epoxy resin takes place.

For this task the anhydride as the modifying agent providing silica surface groups able to interact covalently with epoxy resin was used. It should be noted that modified silica particles with anhydride surface groups can play the role of multifunctional curing agent for epoxy resin.

In the case of anhydride as modifier there are two ways of curing. The first one is providing a chemical reaction between modifier and OH- groups located on the surface of nanoparticles and as a next step - providing curing process by anhydride groups (i.e. in this case the nanoparticles act as multifunctional curing agent):

\[
T_g = \frac{\sum_{i} \Delta V_i}{\left(\sum_{i} a_i \Delta V_i + \sum_{j} b_j \right)_{i,ch} + \left(\sum_{i} K_i \Delta V_i \right)_{\text{cat.p.}}} - \frac{2.377 \times 10^{-8}}{R_{av, np}} \sum_{n} f(R_{np}).
\]  
(20)

Table 1. Physical characteristics of the epoxy resin cured with anhydride-modifier curing agents.

| Physical characteristic                               | Value |
|-------------------------------------------------------|-------|
| Glass transition temperature, $T_g$, K                | 722   |
| Van-der-Waals volume, $\sum \Delta V_i$, Å\(^3\)      | 485   |
| Molecular weight of the repeat fragment, $M_{rf}$      | 535   |
| Thermal coefficient of volumetric expansion, CTE×10\(^4\) K\(^{-1}\) | 1.33  |

Figure 1 demonstrate, as an example, the Poisson’s distribution, expected mean value is equal to $R_{av} = 10$.

Figure 2 demonstrates the dependencies of the glass transition temperature on the expected mean radius of nanoparticles. It can be seen that in the case of small radii of nanoparticles the dependence of the glass transition temperature $T_g$ on $R_{av, np}$ is quite noticeable, especially when the hydrogen bonds take place.
Figure 1. Poisson’s distribution, expected mean value is equal to $R_{av} = 10$.

Figure 2. The dependencies of the glass transition temperature on the expected mean radius of nanoparticles. 1 – expected mean value 5 nm, dipole-dipole interaction; 2 – expected mean value 5 nm, hydrogen bonds; 3 – expected mean value 10 nm, dipole-dipole interaction; 4 – expected mean value 10 nm, hydrogen bonds.

So, we have a situation when a part of epoxy resin will be cured with usual anhydride and another part of epoxy resin will be cured with anhydride-modifier. Then the glass transition temperature is calculated as for the copolymer [12-15]:

\[
\begin{align*}
\text{H} & \text{H} \\
\text{O} & \text{H} \\
\text{O} & \text{H} \\
\text{H}_3\text{C} &
\end{align*}
\]
\[
T_g = \frac{\alpha_1 \left[ \sum_i \Delta V_i \right] + \alpha_2 \left[ \sum_i \Delta V_i \right]}{\alpha_1 \left[ \sum_i a_i \Delta V_i \right] + \sum_j b_j + \sum_i K_i \Delta V_i + \alpha_2 \left[ \sum_i a_i \Delta V_i \right] + \sum_j b_j + \sum_i K_i \Delta V_i},
\]

where \(\alpha_1\) and \(\alpha_2\) are the molar parts of the network 1 (epoxy resin cured with usual anhydride) and 2 (epoxy resin cured with anhydride-modifier); \(\left[ \sum_i \Delta V_i \right]_1\) and \(\left[ \sum_i \Delta V_i \right]_2\) are the Van-der-Waals volumes of the repeating fragments of the networks 1 and 2; \(\left[ \sum_i a_i \Delta V_i \right] + \sum_j b_j + \sum_i K_i \Delta V_i\) and \(\left[ \sum_i a_i \Delta V_i \right] + \sum_j b_j + \sum_i K_i \Delta V_i\) are the sets of atomic constants for the repeating fragments of the networks 1 and 2.

In order to form a modifier's monolayer on the surface of each nanoparticles, the required concentration of modifier \(c_m\) is calculated in accordance with the equation (15). Since \(M_m = 304\), \(c_{np} = 0.1\), \(\left( \sum_i \Delta V_i \right)_m = 290 \text{ Å}^3\), \(\rho = 0.74 \text{ g/cm}^3\), from equation (15) obtain:

\[
c_m = 0.3/R_{np}.
\]

If a Poisson's distribution takes place, this formula is transformed into the equation

\[
c_m = 0.3 \sum_{x=1}^{x_{av}} f(R_{np}) \frac{1}{R_{np}}.
\]

Now, taking into account that for curing of the epoxy resin two molecules of anhydride-modifier are required, we should write

\[
\alpha_2 = \frac{2 c_m M_{ex}}{c_{ex} M_m}.
\]

For our products \(M_{ex} = 252\), \(c_{ex} = 1 - c_{np} - c_m\), \(M_m = 304\). Then

\[
\alpha_2 = 1.658 \frac{c_m}{1 - c_{np} - c_m}.
\]

\[
\left[ \sum_i a_i \Delta V_i \right] + \sum_j b_j + \sum_i K_i \Delta V_i = 1.194 \quad \text{and} \quad \left[ \sum_i a_i \Delta V_i \right] + \sum_j b_j + \sum_i K_i \Delta V_i = 0.67 \quad \text{(calculated using the software CASCADE, INEOS RAS)}.
\]

Then, using the equations (21), (22), and (24), we obtain the dependencies of the glass transition temperature on the expected mean radius \(R_{av, np}\) of nanoparticles. These dependencies are shown on Figure 3.
Figure 3. The dependencies of the glass transition temperature on the average radius of nanoparticles.
1 – expected mean value 5 nm, chemical interaction between the epoxy resin and anhydride-modifier;
2 – expected mean value 10 nm, chemical interaction between the epoxy resin and anhydride-modifier.

The coefficient of thermal expansion is correlated with the glass transition temperature in accordance with the relations listed in the monographs [12-15]. The dependencies of the CTE-values and the expected mean radius $R_{av, np}$ of nanoparticles are shown on Figures 4 (dipole-dipole interactions and hydrogen bonds). It can be seen, the higher the glass transition temperature, the lower CTE-value. The CTE-values also depend on the form of size distribution for nanoparticles.

Figure 4. Dependencies of the coefficients of thermal expansion on the average radii of the nanoparticles. 1 – expected mean value 5 nm, dipole-dipole interaction; 2 – expected mean value 5 nm, hydrogen bonds; 3 – expected mean value 10 nm, dipole-dipole interaction; 4 – expected mean value 10 nm, hydrogen bonds.

4. Conclusion
The expression for the theoretical estimation of $T_g$ value of nanocomposites was modified in order to account for the polydispersity of nanoparticles. The theoretical estimation shows that the influence of the size distribution of the silica nanoparticles on the both $T_g$ and CTE values of the epoxy/silica
nanocomposite can be quite considerable. The most significant effect will be achieved at the conditions, when nanoparticles play the role of multifunctional curing agent.

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