Prediction of the coefficient of thermal expansion of building materials based on polyvinyl chloride

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Abstract: The possibility of predicting the coefficient of thermal expansion for the blends of polyvinyl chloride (PVC) with a number of organic polymers is shown. It was found that the higher the glass transition temperature of the polymer, the lower the coefficient of thermal expansion of the mixture of PVC with this polymer. The dependence of thermal expansion for composites based on wood of different species and bamboo is also analyzed. In all cases, the coefficient of thermal expansion is reduced, which allows the use of forecasting results for the development of new PVC-based building materials with improved thermal properties.

1. Introduction
Polyvinyl chloride (PVC) is one of the most common polymers for building materials. These materials contain PVC in plasticized form, as components of mixtures with wood and other fillers. Wood-polymer composites (WPC), which serve as the basis for terrace boards, siding and other products, are popular [1]. One of the tasks of improving the properties of PVC-based building materials is to reduce the coefficient of thermal expansion, since these materials are used in large quantities for external use. They experience intense heat in the sun. Having a large coefficient of linear or volumetric thermal expansion, the materials lose their performance due to unacceptable resizing.

This work is devoted to theoretical and experimental analysis of the coefficient of linear thermal expansion (CLTE) associated with the prediction of this value for materials based on blends of PVC with other polymers. First of all, we consider the relationship between the CLTE and the thermal characteristics such as the softening temperature and the temperature of the onset of intense thermal degradation of polymers.

2. Softening point
For amorphous systems, the softening temperature of the material is determined by the glass transition temperature of the polymer $T_g$. According to [2-8], the value of $T_g$ for linear polymers is calculated by the equation
where $a_i$ is the set of atomic constants associated with the energy of the weak dispersion interaction and characterizing the average contribution of each atom to this interaction; $b_j$ is the set of increments associated with the energy of a strong specific intermolecular interaction (dipole-dipole, hydrogen bonds, etc.). The constants $a_i$ and $b_j$ are also given in [2–6].

For copolymers, the glass transition temperature is calculated by the ratio:

$$T_g = \frac{\sum_{i} \Delta V_i}{\sum_{j} a_i \Delta V_i + \sum_{j} b_j},$$

(1)

where $T_g$ is the glass transition temperature of the copolymer according to formula (2), it is not necessary to know the experimental values of the glass transition temperatures of homopolymers.

Another way to write a formula is as follows:

$$T_g = \frac{\sum_{k=i}^{k=\text{av}} \alpha_k \left( \sum_{i} \Delta V_i \right)}{\sum_{k=i}^{k=\text{av}} \alpha_k \left( \sum_{i} \Delta V_i + \sum_{j} b_j \right) + 0.03 \sum_{k=i}^{k=\text{av}} \alpha_k (1 - \alpha_k)},$$

(2)

where $\alpha_k$, $\left( \sum_{i} \Delta V_i \right)_k$ and $\left( \sum_{i} \Delta V_i + \sum_{j} b_j \right)_k$ is the mole fraction of the van der Waals volume and the set of atomic constants and increments for the $k$-th component, respectively.

In order to calculate the glass transition temperature of the copolymer according to formula (2), it is not necessary to know the experimental values of the glass transition temperatures of homopolymers.

In the calculations according to formula (4), both calculated and experimental values of $T_{g,k}$ can be used.

3. The temperature at the beginning of intense thermal destruction

Experimentally, this characteristic $T_d$ is determined by the intersection of the tangents to the two branches of the thermogravimetric curve. It is calculated from the ratio [2-5]

$$T_d = \frac{\sum_{i} \Delta V_i}{\sum_{i} K_i \Delta V_i},$$

(4)

where $K_i$ are the atomic constants associated with the parameters of the Morse potential; $K_i = \frac{63}{2} \frac{R}{(a d_i) E}$, $a$ and $d_0$ are the parameters of the Morse potential, $E$ is the chemical bond energy.

The glass transition temperature of cross-linked polymers is calculated according to the equation [2-5]

$$T_g = \frac{\sum_{i} \Delta V_i}{\left( \sum_{i} a_i \Delta V_i + \sum_{j} b_j \right)_x + \left( \sum_{i} K_i \Delta V_i \right)_y},$$

(5)
where \( \sum_i \Delta V_i \) is the van der Waals volume of the repeating fragment of the polymer network; 
\[
\left( \sum_i a_i \Delta V_i + \sum_j b_j \right)
\]

is the set of atomic constants for linear chains connecting the cross-linked points; 
\[
\left( \sum_i K_i \Delta V_i \right)
\]

is the set of constants for the cross-linked points (the physical meaning of the parameters \( a_i, b_i \), and \( K_i \) is the same as in equations (1) and (4)).

According to [2–5], the network cross-linked point is a group of atoms, including the atom from which the branching occurs, plus neighboring atoms chemically bonded to it with their nearest substituents.

The results of the calculation of the CLTE are shown in Table 1 for a number of polymers that can be combined with PVC or form technological mixtures with this polymer. The chemical structures of lignins and hemicelluloses are borrowed from monograph [9]. In all cases, the polymers shown in Table 1 reduce the CLTE value when mixed with PVC.

**Table 1.** The calculated properties of the polymers

| Structure                                | \( V_m \, \text{cm}^3/\text{mol} \) | \( \delta \, (\text{J/cm}^3)^{0.5} \) | \( \gamma \, \text{mN/m} \) | \( T_g \, \text{K} \) | \( T_d \, \text{K} \) | \( \alpha_G \, \text{K}^{-1} \cdot 10^4 \) | \( \alpha_L \, \text{K}^{-1} \cdot 10^4 \) |
|------------------------------------------|-------------------------------------|---------------------------------------|------------------|-----------------|-----------------|-----------------|-----------------|
| Polyvinyl chloride                       | 43.3                                | 19.4                                  | 34.2             | 340             | 530             | 2.81             | 0.94             |
| Cellulose                                | 116                                 | 31.4                                  | 52.2             | 540             | 550             | 1.78             | 0.59             |
| Hemicellulose (averaged values for 16 hemicelluloses) | 230                                 | 27.7                                  | 48.3             | 474             | 540             | 1.94             | 0.65             |
| Lignin ate 1                             | 342                                 | 25.3                                  | 45.2             | 480             | 610             | 2.00             | 0.67             |
| Lignin ate 2                             | 342                                 | 21.6                                  | 25.4             | 440             | 580             | 2.16             | 0.72             |
| Beech lignin 1                           | 334                                 | 23.0                                  | 36.8             | 460             | 590             | 2.10             | 0.70             |
| Beech lignin 2                           | 331                                 | 23.7                                  | 39.6             | 520             | 529             | 1.85             | 0.62             |
| Poly-4-chlorostyrene                     | 109                                 | 19.6                                  | 34.4             | 410             | 550             | 2.34             | 0.78             |
| Poly-2,6-Dichlorostyrene                 | 121                                 | 20.4                                  | 38.4             | 405             | 515             | 2.37             | 0.79             |
| Polycarbonate                            | 211                                 | 19.4                                  | 33.0             | 431             | 717             | 2.23             | 0.74             |
| Polymide ULTEM                            | 460                                 | 20.6                                  | 37.4             | 500             | 730             | 1.91             | 0.64             |
| Polyetheretherketone                     | 232                                 | 19.9                                  | 35.3             | 420             | 780             | 2.31             | 0.77             |
| Polyeatherketone                         | 157                                 | 20.3                                  | 36.9             | 430             | 760             | 2.23             | 0.74             |
| Polysulfone                              | 353                                 | 21.0                                  | 38.8             | 467             | 679             | 2.05             | 0.68             |
| Polyphenylene sulfide                    | 83.5                                | 20.9                                  | 69.0             | 363             | 726             | 2.64             | 0.88             |
| Poly-2,6-dimethylphenylene oxide         | 104                                 | 18.3                                  | 48.9             | 442             | 703             | 2.17             | 0.72             |
| Polyaurylate F-2                         | 345                                 | 21.0                                  | 39.6             | 578             | 683             | 1.67             | 0.56             |

The following values are entered in the table: \( V_m \) is the molar volume, \( \delta \) is the solubility parameter, \( \gamma \) is the surface energy, \( T_g \) is the glass transition temperature, \( T_d \) is the temperature of the onset of intense thermal degradation, \( \alpha_G \) is the coefficient of volumetric thermal expansion, \( \alpha_L \) is the coefficient of linear thermal expansion.

**4. Experimental evaluation of softening temperature and coefficient of linear thermal expansion (CLTE)**

**4a. Thermomechanical curves (TM-curves)**

TM curves were measured on a TMA Q400 instrument (TA Instruments). The tests were carried out under conditions of penetration of the punch into a cylindrical sample with an increase in temperature.
of 5 deg/min. The diameter of the punch was 2.5 mm, the load on the punch was 100 g. As an example, the TM curve for the sample containing 40% PVC and 60% wood is shown in Figure 1.

![TM curve and derivative of the deformation of the sample containing 40% PVC and 60% wood. In the upper left corner, the derivative with respect to deformation in the temperature range 60-90 °C is shown.](image)

Figure 1. TM curve and derivative of the deformation of the sample containing 40% PVC and 60% wood. In the upper left corner, the derivative with respect to deformation in the temperature range 60-90 °C is shown.

The softening temperature characterizing the deformation resistance falls into the range of 170-180°C. The temperature of the maximum strain growth rate is 214-218°C.

4b. Linear thermal expansion coefficients
The CLTE values were measured in different directions of the terrace boards. CLTE $\alpha$ was calculated by the following ratio:

$$\alpha = \frac{I_T - I_0}{I_0 \cdot (T - T_0)}$$

where $I_0$ is the initial size of the sample, $I_T$ is the size of the sample after heating, $T_0$ is the initial temperature, $T$ is the final heating temperature.

The CLTE values were determined in two ways. In the first of them, an experiment was conducted to measure the size of a sample with a very small load on the punch, equal to 0.5 g, on the TMA Q400 instrument (TAInstruments). As an example, the temperature dependence of the change in size of the above sample is shown in Figure 2 over the entire temperature range studied.
Figure 2. The dependence of the change in the size of sample 2 (see Table 2) on temperature and the value of the CLTE in different temperature ranges

It is known that even for a homogeneous polymer in a glassy state, the CLTE is not constant and depends on the temperature range in which it is measured. On the TMA Q400 instrument (TAInstruments) using a computer program built into this instrument, the CLTE is determined automatically. The temperature intervals in which the CLTE remains constant, and the value of this coefficient, measured in μm/m·deg, is displayed on the diagram (Fig. 2). For this sample, the CLTE value in the temperature range from 19 to 40°C is $0.478 \times 10^{-4} \text{ K}^{-1}$. This value is typical for amorphous polymers and below the coefficient of thermal expansion of PVC, which is $0.94 \times 10^{-4} \text{ K}^{-1}$.

In the second method, the length, width and thickness of the samples were measured at 18°C using a caliper equipped with an electronic reference system; the measurement accuracy was 0.01 mm. Further, these samples were placed in a heating cabinet and maintained at the temperature of 70°C for 1.5 hours. After that, the samples were sequentially removed from the oven, and their surface temperature was measured with an ADA Instruments TemPro 550 pyrometer.

For a detailed analysis of the coefficient of linear thermal expansion (CLTE) on the TMA Q400 instrument (TAInstruments), an experiment was conducted to measure the size of the sample with a very small load on the punch, equal to 0.005N. The temperature dependence of the change in sample size is shown in Figure 2 over the entire temperature range studied.

The material we consider in this article contains 40% PVC and 60% wood. For polymers, the value of the coefficient of volumetric thermal expansion $\alpha_V$ is calculated by the formula (2-5):

$$
\alpha_V = \frac{\sum_i \alpha_i \Delta V_i + \sum_j \beta_j}{\sum_i \Delta V_i},
$$

where $\alpha_i$ are the partial coefficients of volumetric thermal expansion due to the weak dispersion interaction of the $i$-th atom with neighboring atoms, $\beta_j$ are the parameters characterizing the contribution of each type of specific intermolecular interaction (dipole-dipole, hydrogen bonds) to the coefficient of thermal expansion.

The values of the constants $\alpha_i$ and $\beta_j$ for a number of atoms and types of intermolecular interactions are given in [2-4]. For copolymers and compatible polymer blends, the coefficient of linear thermal expansion $\alpha_L$ is calculated by the formula (taking into account that $\alpha_L = \alpha_V/3$):
where $\alpha_k$ is the mole fraction of component $k$, $n$ is the number of components.

If it is necessary to express the thermal coefficient of linear expansion of the copolymer in terms of thermal coefficients for the corresponding copolymers, it is necessary to write

$$\alpha_L = \frac{1}{3} \sum_{k=1}^{n} \alpha_k \left( \sum_{j} \alpha_j \Delta V_j + \sum_{j} \beta_j \right),$$

where $\alpha_{G,k}$ is the thermal coefficient of volume expansion of the $k$-th component of the copolymer.

The average CLTE values for the temperature range of interest from -30 to 50°C are shown in Table 2. Considering that the CLTE value for PVC is $94\cdot10^{-6}$ $^1\text{C}$, we can conclude that the introduction of wood into the composite reduces the CLTE value. Calculations show that the CLTE when filling PVC with ordinary spruce wood is $76,6\cdot10^{-6}$ $^1\text{C}$, which is close to the experimental value. The estimated value for a mixture of PVC with moso bamboo, which is the most basic kind of bamboo in China, is $70,8\cdot10^{-6}$ $^1\text{C}$, which is less than when filling with spruce wood.

**Table 2.** The averaged values of the CLTE in the range of operating temperatures for the samples of WPC (1) - (6) in parallel measurements

| Composition | CLTE, $\alpha_{cp} \cdot 10^{-6}$, in the range of operating temperatures $-30 \div 50$ °C |
|-------------|-----------------------------------------------------------------------------------|
| 1           | 75                                                                                |
| 2           | 59                                                                                |
| 3           | 76                                                                                |
| 4           | 69                                                                                |
| 5           | 71                                                                                |
| 6           | 60                                                                                |

4c. **CLTE measurements of universal bars from DPC**

According to the second method, the measurements were carried out as follows: samples of universal bars with dimensions of $7\times7\times4$ cm were measured in length and width at 18°C using a caliper equipped with an electronic reference system. Further, these samples were placed in a heating cabinet and kept to a temperature of 50°C for 1.5 hours. After that, the samples were sequentially removed from the oven, and their surface temperature was measured with an ADA Instruments TemPro 550 pyrometer. The dimensions of the samples along the length and width, which increased as a result of increasing material temperature, were also measured. The measurements were carried out in different places of each sample (in the middle of the rib, at the location of the reinforcing rib). The introduction of calcite (chalk) in the composition of DPC decreases CLTE even more, since for the rhombohedral structure of calcite the CLTE is $25\cdot10^{-6}$ $^1\text{C}$ along the axis of the crystal and $-5,6\cdot10^{-6}$ $^1\text{C}$ perpendicular to this axis. The measurements performed in this work showed that the dependences of the coefficient of linear thermal expansion along the length, width, and thickness of terrace boards on the percentage of chalk look like that shown in Figure 3.
Figure 3. Dependences of the coefficient of linear thermal expansion along the length (1), width (2), and thickness (3)

5. Conclusion
The possibility of predicting the coefficient of thermal expansion of materials based on blends of polymers with PVC is shown. The calculations showed that there are many polymer structures that combine with PVC or form technological blends. All these systems possess a lower CLTE value compared to the original PVC. Lowering reaches from 6 to 52%. The higher the glass transition temperature of the polymer introduced into the mixture with PVC, the greater the decrease in CLTE. The introduction of a mineral filler in the composition of the mixtures also lowers the value of the CLTE as a function of its content. Experiments and calculations were performed for wood-polymer composites. It is shown that the value of CLTE during filling with a bamboo wood [10] decreases to a greater extent than when filling with coniferous wood.

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