Rheological properties of the polymeric blends

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Abstract. The calculation scheme for storage modulus and loss modulus for compatible polymers as a function of the temperature, stress state, and composition has been suggested. The relations for calculation of the storage modulus at high frequency for polymer of any chemical structure containing carbon, hydrogen, and oxygen atoms are suggested. Calculation scheme allows evaluation both of the storage modulus and loss modulus for compatible blends of polymers. The calculations are performed for mixtures of polystyrene, poly(methyl methacrylate), polycarbonate, and polyethylene oxide used for the manufacture of building materials.

1 Introduction

Within the frame of the papers [1] it was shown that the storage modulus at high frequencies is described by the following equation

$$G = \frac{\sum_i \Delta V_i}{\sum_i g_i \Delta V_i + \sum_j f_j}, \quad (1)$$

where $g_i = \frac{S_i}{k_i l_i}$; the values of g_i characterize an average contribution of each atom into the value of $\frac{S_i}{k_i l_i}$; f_i is the selection of constants which characterize the influence of strong intermolecular interaction (dipole-dipole interaction, hydrogen bonds, etc.); S_i is the Van-der-Waals surface of the i-th atom, through which the intermolecular interaction occurs; κ_i is the elasticity coefficient of the i-th atom bond; l_i is the characteristic size of the bond; $\sum_i \Delta V_i$ is the Van-der-Waals volume of i-th atom entering into repeating unit of polymer.

For compatible blend of polymers the equation (1) is transformed to the form:

$$G = \frac{\alpha_1 \left(\sum_i \Delta V_i \right)_1 + \alpha_2 \left(\sum_i \Delta V_i \right)_2}{\alpha_1 \left(\sum_i g_i \Delta V_i + \sum_j f_j \right)_1 + \alpha_2 \left(\sum_i g_i \Delta V_i + \sum_j f_j \right)_2}, \quad (2)$$

where α_1 and α_2 are the molar parts of polymer 1 and 2, respectively;

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$\left(\sum_i g_i \Delta V_i + \sum_j f_j\right)_1$ and $\left(\sum_i g_i \Delta V_i + \sum_j f_j\right)_2$ are the selections of constants for the polymer 1 and 2, respectively.

Taking into account that in accordance with the equation (1) the values of $\left(\sum_i g_i \Delta V_i + \sum_j f_j\right)$ is equal to $\left(\sum_i g_i \Delta V_i + \sum_j f_j\right) = \frac{\sum_i \Delta V_i}{G}$ we can rewrite the equation (2) as:

$$G = \frac{\alpha_1 \left(\sum_i \Delta V_i\right)_1 + \alpha_2 \left(\sum_i \Delta V_i\right)_2}{\alpha_1 \frac{\left(\sum_i \Delta V_i\right)_1}{G_1} + \alpha_2 \frac{\left(\sum_i \Delta V_i\right)_2}{G_2}}, \tag{3}$$

where G_1 and G_2 are the moduli of the component 1 and 2, respectively. Because $\alpha_1+\alpha_2=1$, obtain:

$$G = \frac{\left(\sum_i \Delta V_i\right)_1 + \alpha_2 \left[\left(\sum_i \Delta V_i\right)_2 - \left(\sum_i \Delta V_i\right)_1\right]}{\frac{\left(\sum_i \Delta V_i\right)_1}{G_1} + \alpha_2 \left[\frac{\left(\sum_i \Delta V_i\right)_2}{G_2} - \frac{\left(\sum_i \Delta V_i\right)_1}{G_2}\right]}. \tag{4}$$

The equation (4) allows description of the shear modulus G depending on molar concentration of Polymer 2.

Let us examine the example of calculation using the polymers used in the building industry. It is well known that fully compatible blend of polymers is as following: "polystyrene + polycarbonate". The Table 1 of the values g_i and f_j is borrowed from the paper [1]:

Table 1. Values of constants g_i and f_j

Atom or type of intermolecular interaction	Values of g_i or f_j	
Carbon	g_C, cm^2/kg	-1.277
Hydrogen	g_H, cm^2/kg	4.376
Oxygen	g_O, cm^2/kg	116.95
Double bond	$f_{\neq}$, Å^{3}cm^2/kg	30.925
Dipole-dipole interaction*	f_d, Å^{3}cm^2/kg	84.472

** Parameter f_d is introduced for each branching in the back bone or side chain. This parameter is introduced also in the presence of a polar group of any type.*

Using these parameters as well as the Van-der-Waals volumes of the atoms [2-5] we obtain for polystyrene $\left(\sum_i g_i \Delta V_i + \sum_j f_j\right)_{PS} = -1.277(13.1+8.7+8.4+5\cdot 12.7)+4.376(8\cdot 2.0)+84.472=34.8$. Van-der-

Waals volume of Polystyrene is $\left(\sum_i \Delta V_i\right)_{PS}$ = 110 Å^3 (calculations are produced by the software Cascade). So, the value of storage modulus is G_{PS} = 3.15 kg/cm^2 (it should be noted that the experimental value of G = 3.16 kg/cm^2).

For polycarbonate $\left(\sum_i g_i \Delta V_i + \sum_j f_j\right)_{PC}$ = –1.277(4·16.9+6·8.4+2·11.6+4·12.7+4.5+ +2·12.7+19.0)+4.376(22·2.0)+116.95(2·2.7+5.95)+84.472 = 1285.3. Van-der-Waals volume of polycarbonate is $\left(\sum_i \Delta V_i\right)_{PC}$ = 305.3 Å^3. So, the value of storage modulus is G_{PC} = 0.24 kg/cm^2. The dependence of storage modulus of the blend under consideration on the molar part of polycarbonate is shown on Figure 1.

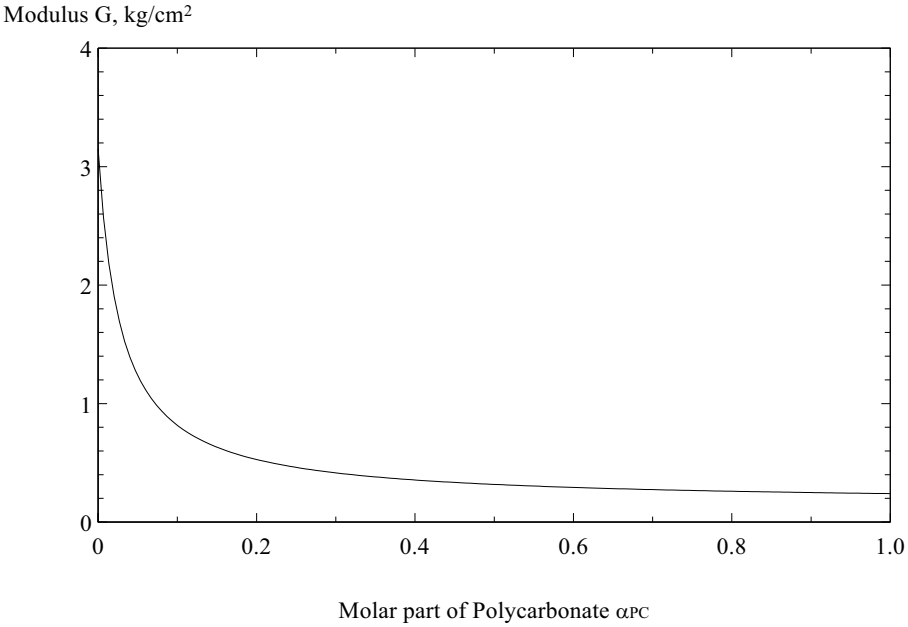

Fig.1. Dependence of storage modulus on the molar fraction of polycarbonate.

The major curvature of the dependence is due to the great difference between the Van-der-Waals volumes of the components.

The other compatible blend is "poly(ethylene oxide) + poly(methyl methacrylate)". For poly(ethylene oxide) $\left(\sum_i g_i \Delta V_i + \sum_j f_j\right)_{PEO}$ = –1.277(2·16.2)+4.376(4·2.0)+116.95·3.4= =391.26 cm^2/kg·Å^3. Van-der-Waals volume of poly(ethylene oxide) $\left(\sum_i \Delta V_i\right)_{PEO}$ = 43.7 Å^3. So, the value of storage modulus is G_{PEO} = 0.112 kg/cm^2. For poly(methyl methacrylate) $\left(\sum_i g_i \Delta V_i + \sum_j f_j\right)_{PMMA}$ = –1.277(13.1+5.0+17.2+15.9+20.3)+4.376(8·2.0)+116.95(5.85+ +3.4)+84.472·2=1229 cm^2/kg·Å^3. Van-der-Waals volume of poly(methyl methacrylate)

$\left(\sum_i \Delta V_i\right)_{PMMA}$ = 96.4 Å^3. So, the value of storage modulus is G_{PMMA} = 0.08 kg/cm^2.

The dependence of storage modulus of this blend on the molar part of poly(methyl methacrylate) is shown on Figure 2.

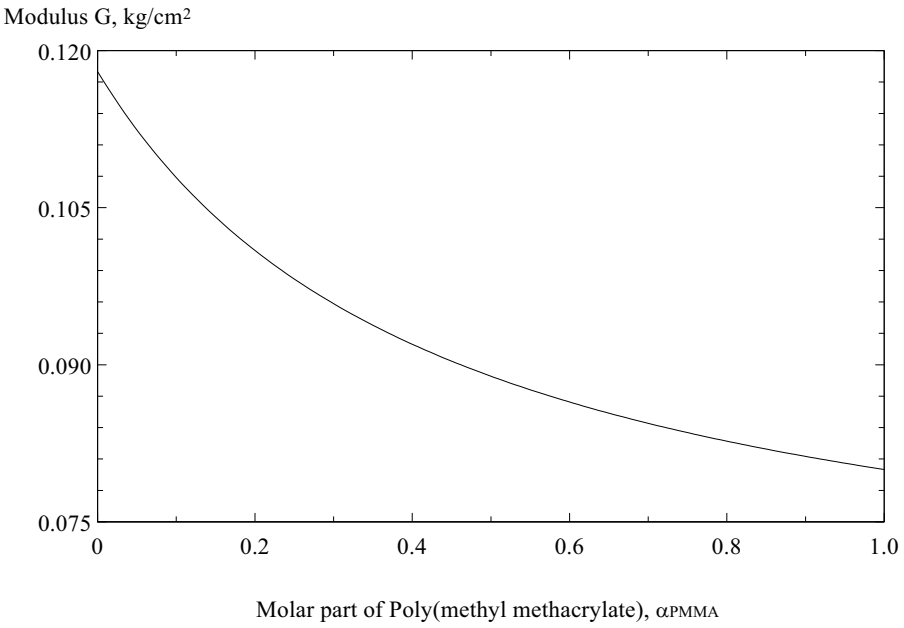

Fig.2. Dependence of storage modulus on the molar part of poly(methyl methacrylate)

It is well known that molar α_m and weight α_w fractions are related by

$$\alpha_m = \frac{1}{1+\frac{M_2}{M_1}\left(\frac{1}{\alpha_w}-1\right)}, \tag{5}$$

where M_1 and M_2 are the molecular weights of the repeating units of polymer 1 and polymer 2, respectively.

The dependence of the storage modulus on the weight part $\alpha_{w,2}$ of the polymer 2 is described by the following formula

$$G = \frac{\left(\sum_i \Delta V_i\right)_1 + \frac{\left[\left(\sum_i \Delta V_i\right)_2 - \left(\sum_i \Delta V_i\right)_1\right]}{1+\frac{M_2}{M_1}\left(\frac{1}{\alpha_{w,2}}-1\right)}}{\frac{\left(\sum_i \Delta V_i\right)_1}{G_1} + \frac{\left[\frac{\left(\sum_i \Delta V_i\right)_2}{G_2} - \frac{\left(\sum_i \Delta V_i\right)_1}{G_1}\right]}{1+\frac{M_2}{M_1}\left(\frac{1}{\alpha_{w,2}}-1\right)}}. \tag{6}$$

For poly(ethylene oxide) M_{PEO} = 44.1; for poly(methyl methacrylate) M_{PMMA} = 100; for polystyrene M_{PS} = 104; for polycarbonate M_{PC} = 310. Substituting all the physical

parameters mentioned above obtain the dependence of storage modulus on the weight part of poly(methyl methacrylate) (Figure 3):

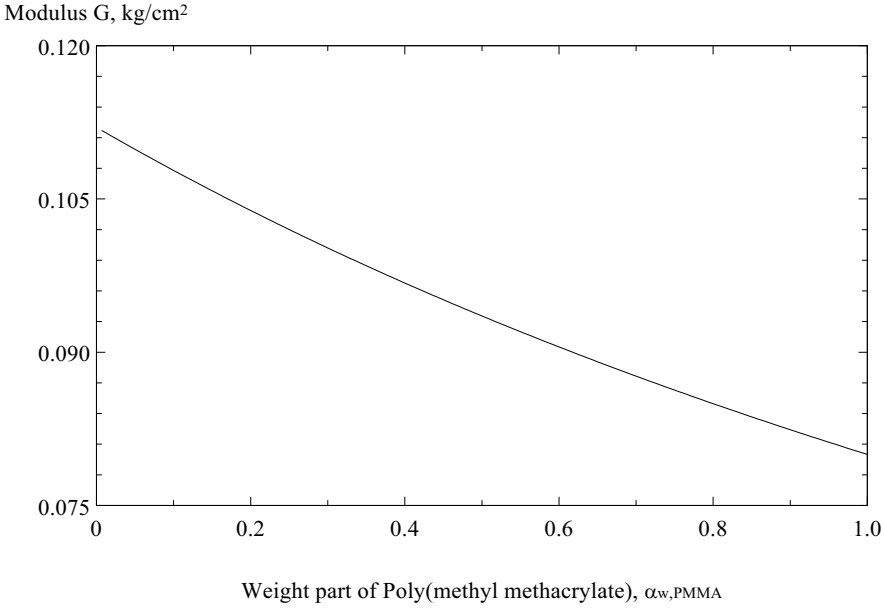

Fig.3. Dependence of storage modulus on the weight part of poly(methyl methacrylate).

The dependence of storage modulus on the weight part of polycarbonate is shown on Fig. 4.

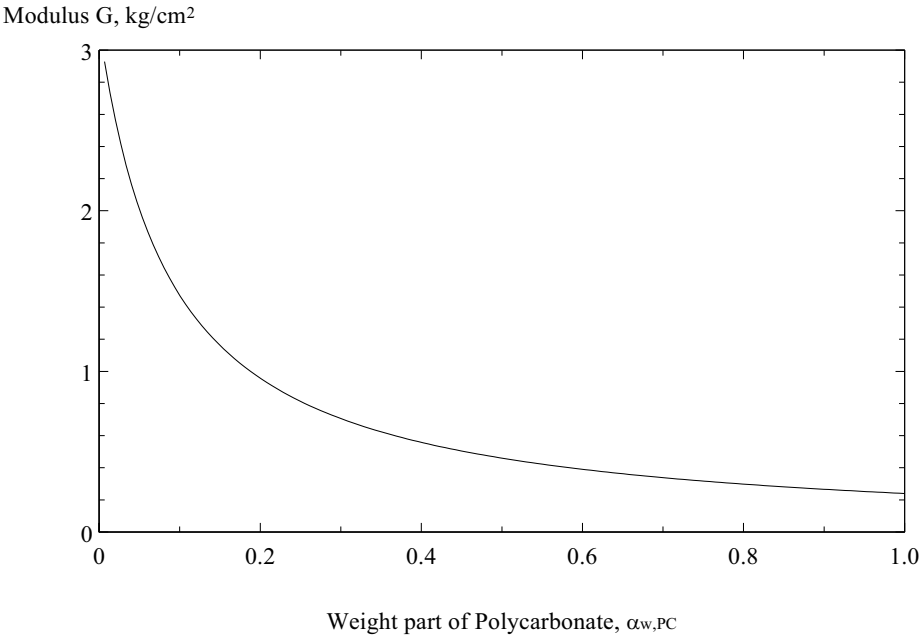

Fig.4. Dependence of storage modulus on the weight part of polycarbonate $\alpha_{w,PC}$.

The storage modulus and loss modulus of the polymer blends

Now we consider the calculation of storage and loss moduli $G'(\omega)$, $G''(\omega)$ of the polymer blends. It is well-known that in the Maxwell regime (i.e., when there is a single typical relaxation time τ) the storage an loss moduli are given by the following formulae

$$G'(\omega) = G\frac{(\omega\tau)^2}{1+(\omega\tau)^2}, \tag{7}$$

$$G''(\omega) = G\frac{(\omega\tau)}{1+(\omega\tau)^2}, \tag{8}$$

where G is the high-frequency limit of the storage modulus and the relaxation time τ is given by

$$\tau = \frac{\eta}{G\Gamma\left(1+\frac{1}{k}\right)}, \tag{9}$$

where $\Gamma(x)$ is the Euler gamma function, and the parameter k is due to the non-exponential relaxation in polymer systems.

As an example of calculations we consider a mixture of poly(ethylene oxide) and poly(methyl methacrylate). Using values $\left(\sum_i \Delta V_i\right)_{PMMA}$, $\left(\sum_i \Delta V_i\right)_{PEO}$, G_{PMMA}, and G_{PEO} for these polymers, the resulting dependencies on the concentration of PEO are given in Table 2.

Table 2. The values of modulus G for the compatible blends of PEO and PMMA.

α_{PEO},%	α_{PMMA},%	G, N/ m^2
0	100	8000
20	80	8240
40	60	8570
60	40	9050
80	20	9810
100	0	11200

Viscosity of the mixtures calculated by Bicerano method [6] as a function of temperature is given in Table 3.

Consider first the temperature dependence of the storage and loss moduli. Assume, for definiteness, that $\alpha_{PEO} = 40\%$, $\alpha_{PMMA} = 60\%$, and the weight average molecular weight to be $M_w = 40000 g/mol$. Then the high frequency storage modulus is $G = 8570\,\mathrm{N/m^2}$ and the relaxation time as a function of temperature is given in the Table 3.

Table 3. The values of $\eta_{\square}$ and τ at various temperatures.

T, K	400	415	430	445	460	475
η_0, N·sec/m^2	1387974	105633	283	147	79	45
τ, sec	81.0	6.16	0.0165	0.00855	0.00463	0.00262

The corresponding frequency dependences both of the storage and loss moduli are presented in Figure 5. Storage moduli are plotted in full lines, and loss moduli are in dashed lines.

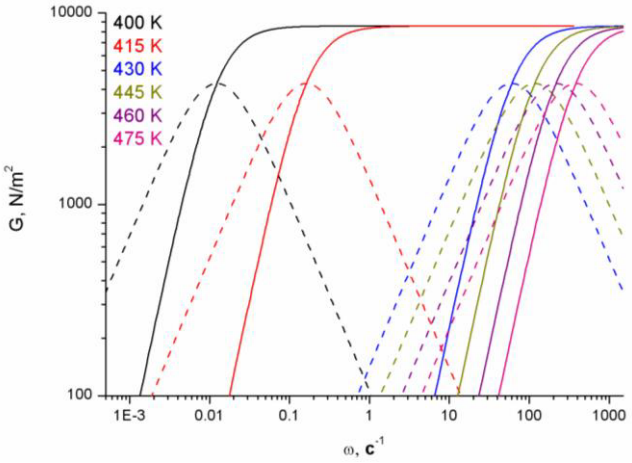

Fig.5. The dependencies of storage (*G*') and loss moduli (*G*'') on frequency at various temperatures.

To study the concentration dependence of the moduli, assume T = 445 K, and, once again $M_w = 40000 g/mol$. Then, depending on the composition of the blend one has the following results for the high frequency storage modulus, the viscosity, and the relaxation time are given in Table 4.

Table 4. The values of G, η_0 and τ at various concentrations of the components.

α_{PEO},%	0	20	40	60	80	100
G,N/m^2	8000	8240	8570	9050	9810	11200
η_0, N·sec/m^2	130.4	125.0	146.5	245.8	447.7	419.3
T, sec	0.00815	0.00758	0.00855	0.0136	0.0228	0.0187

The corresponding frequency dependences of the storage and loss moduli are presented in Figures 6 and 7. Storage moduli are plotted in full lines, and loss moduli are in dashed lines.

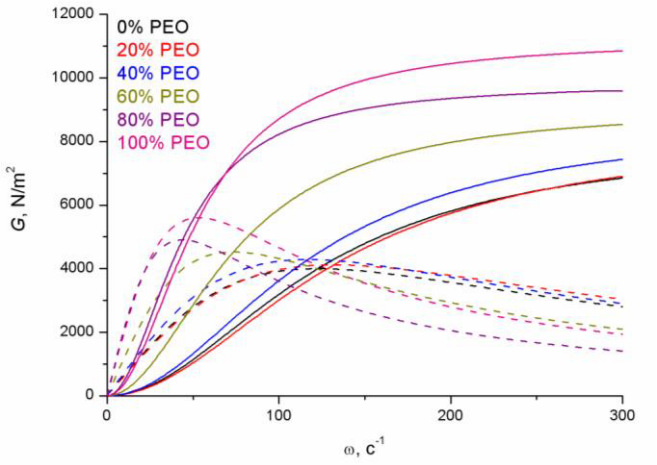

Fig.6.The dependencies of storage (*G*') and loss moduli (*G*'') on frequency at various contents of PEO.

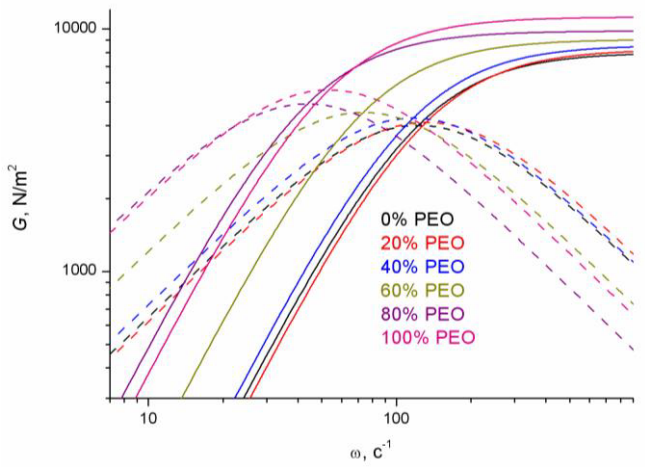

Fig.7. The dependencies of storage (*G*') and loss moduli (*G*") on frequency at various contents of PEO.

Conclusions

The possibility of calculation of the modulus of elasticity at high frequency has been demonstrated. All the physical parameters we need for calculations can be predicted by the software Cascade (INEOS RAS). The dependencies of modulus of elasticity on both the molar and weight part possess various forms depending on the Van-der-Waals volume of the components. The proposed calculation scheme may be useful for predicting the rheological properties of polymeric materials and the search for optimal process conditions of production of building materials.

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