## STRUCTURAL-MECHANICAL AND THERMOPHYSICAL PROPERTIES

OF MODIFIED POLYVINYL CHLORIDE

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On the basis of a systematic investigation of the viscoelastic properties of polyvinyl chloride filled with waste from mineral fertilizer and phosphoric acid production in the form of highly dispersed phospho-gypsum, the specific heat is calculated and the energy of interaction of the structural elements of the system matrix is determined, together with the effective thermal conductivity coefficient, with allowance for energy dissipation by the elements of the structure.

A model experimental approach to the study of general physicochemical problems of the structure and properties of filled polymer systems requires an in-depth analysis of the changes in their energy spectrum and the nature of the kinetic effects under the influence of the ingredients [1]. The main difficulty in investigating the vibrational motion of the structural organization in compositions is the need to solve the molecular physics problem of controlling the stereochemical characteristics of individual subsystems capable of chang-ing shape and in different conformations aggregating into structural elements of higher order [2]. All this is known to be of practical as well as theoretical interest in connection with the investigation of energy transfer processes in these systems under the influence of a mechanical or temperature field [3].

The present research is devoted to the investigation of the effect of structural modification on the dissipative energy losses and the spectral distribution density of the kinetic elements of polyvinyl chloride (PVC) filled with phospho-gypsum (PG). We investigated systems based on PVC MW 1.4 × 10<sup>5</sup> with a Fikentscher constant of 65 obtained by suspension polymerization and purified by reprecipitation from solution. As fillers we used commercial PG with the composition:  $CaSO_4 \cdot 2H_2O - 75 - 79\%$ ;  $H_2O$  (free) - 18-22\%;  $P_2O_5 - 0.97 - 1.8\%$ ; F - 0.8-1.0\%;  $SiO_2 - 0 - 0.5\%$ . The predominant particle fraction was crystals 10 to 40 microns in size. The initially highly dispersed PG was dried at T = 373 K, and then after mechanical mixing with PVC, compositions were obtained in the T-p regime [4]. The temperature and concentration dependence of the density  $\rho$  of the PVC compositions and the longitudinal  $v_{\ell}$  and shear  $v_{t}$  strain rates at 0.4 MHz were determined by the method described in [5].

The real parts of the moduli (E',  $\mu$ ', K') were determined in accordance with [5] using the known values of  $v_{\ell}$  and  $v_t$ , the investigation frequency  $\omega$  and the corresponding absorption coefficients  $\alpha_{\ell}$  and  $\alpha_t$ .

It was found that even at a filler content of 0.1-0.3% by vol. the experimental values of  $\rho$  for the PVC compositions differ from those calculated in accordance with the additive component contribution rule. A "plateau" corresponding to a PG content of 5-10% by vol. is observed on the density-filler content  $\rho-\varphi$  curve. A further increase in the PG content of the system leads to an increase in  $\rho$ .

On the filler concentration range 0.1-1.0% by vol. the density of the polymer matrix  $\rho_M$  also differs from the system density (Fig. 1). When  $\varphi = 7.0\%$  by vol. a maximum of  $\rho_M$  is observed, while on the filler concentration range 8-20% by vol.  $\rho_M$  decreases, which points to a loosening of the matrix.

The change in the  $\rho_M$  of PVC systems under the influence of a filler also finds expression in a change in their viscoelastic properties. As follows from Table 1, the change in the viscoelastic properties of the composition is sharpest on the filler content range from 0.1 to

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Fig. 1. Concentration dependence of the density of PVC systems: 1) PVC+PG (experiment); 2) PVC+PG (additivity); 3) PVC+PG (matrix density).  $\rho$ , kg/m<sup>3</sup>;  $\varphi$ , % by vol.

0.5% by vol. This points not only to a decrease in the mobility of the segments of the macromolecules and supermolecular formations of the PVC but also to structural changes affecting the PVC in the boundary layers [1, 4]. With further increase in the PG content  $\varphi$  of the PVC competing effects associated with the increased polymer fraction in the boundary layer and the stiffening of the structural elements of the polymer are observed.

In order to be able to predict the viscoelastic properties of PVC compositions we calculated them using various methods and models [3, 6-9]. An analysis of the results obtained (Table 1) shows that on the range of filler contents  $\varphi$  from 0 to 0.1% by vol. the most satisfactory agreement between experiment and theory is obtained using the two-component Einstein model [8], while on the interval 0.5-5.0% by vol. the self-consistent field method [6, 7] and the micromechanical theory [8] give the best results. When  $\varphi \ge 5.0\%$  by vol. the theoretical calculations considered do not give satisfactory agreement with experiment.

Starting from the values of  $v_l$  and  $v_t$  we calculated the characteristic frequency spectrum of the PVC systems ( $\omega_0^k$ ,  $\omega_0^t$ ) in accordance with the relations

$$\omega_{\rm D}^{l} = \frac{(6\pi^2 N)^{1/3}}{V^{1/3}} v_l; \ \omega_{\rm D}^{t} = \frac{(6\pi^2 N)^{1/3}}{V^{1/3}} v_l.$$
(1)

As follows from the data of Table 2, as the filler concentration varies, so do the values of  $\omega_D^{0}$  and  $\omega_D^{t}$ . Thus, on the filler concentration range 0.5-1.0% by vol. a maximum of the longitudinal frequencies is observed, while the value of  $\omega_D^{t}$  increases on the concentration interval from 2.0 to 20.0% by vol. A comparison of calculated values of  $\omega_D^{0}$  and  $\omega_D^{t}$  for filled PVC and the calculated spectrum for the initial polymer shows that they are somewhat higher for the system PVC+PG. This points to a stiffening of the polymer structure under the influence of the highly dispersed PG as a result of the formation of a dipole-dipole bond between the structural elements of the PVC and the active centers of the filler [4].

Knowing  $\omega_{\rm L}^0$  and  $\omega_{\rm L}^{\rm L}$ , we can determine the elastic moduli of these elements of the system as a function of the filler concentration. For this purpose we will consider the quasilattice formed by a linear chain of the type ABAB..., in which two different elements with masses M<sub>A</sub> and M<sub>B</sub> (M<sub>A</sub> < M<sub>B</sub>) alternate [10]. We will assume that the simple linear lattice of type A is formed by the group CH<sub>2</sub> (M<sub>A</sub> = 23.284969 × 10<sup>-27</sup> kg) and that of type B by CHCl (M<sub>B</sub> = 80.463721 \cdot 10<sup>-27</sup> kg). If it is assumed that the structural elements are bound together by quasi-elastic forces with elastic constant  $\beta$  and the length of the unit cell is equal to d, then for longitudinal vibrations the solution of the secular equation of the type

$$\left|\frac{M}{(M_A M_B)^{1/2}} \Phi_{A,B} - M\omega^2 \delta_{A,B}\right| = 0,$$
(2)

where  $\Phi_{A,B}$  is the A-B interaction potential, has the form:

$$\omega(k) = \left[\frac{\beta}{M_A M_B} \left\{ M_A + M_B \pm (M_A^2 + M_B^2 + 2M_A M_B \cos{(dk)^{1/2}} \right\} \right]^{1/2}.$$
 (3)

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equationSelf-consistentMicron<math>E'\cdot10^{-e}</math><math>\mu'\cdot10^{-e}</math><math>K'\cdot10^{-e}</math><math>\mu'\cdot10^{-e}</math><math>K'\cdot10^{-e}</math><math>K'\cdot10^{-e}</math><math>E'\cdot10^{-e}</math><math>\mu'\cdot10^{-e}</math><math>K'\cdot10^{-e}</math><math>E'\cdot10^{-e}</math><math>K'\cdot10^{-e}</math><math>K'\cdot10^{-e}</math><math>E'\cdot10^{-e}</math><math>E'\cdot10^{-e}</math><math>E'\cdot10^{-e}</math><math>E'\cdot10^{-e}</math><math>K'\cdot10^{-e}</math><math>K'\cdot10^{-e}</math><math>T,43</math><math>1,55</math><math>5,35</math><math>7,16</math><math>1,45</math><math>5,20</math><math>7,88</math><math>1,70</math><math>5,61</math><math>7,89</math><math>7,64</math><math>1,37</math><math>5,61</math><math>7,23</math><math>1,47</math><math>5,25</math><math>7,72</math><math>1,67</math><math>5,61</math><math>7,89</math><math>7,61</math><math>1,63</math><math>5,61</math><math>7,72</math><math>1,47</math><math>5,25</math><math>7,72</math><math>1,67</math><math>7,78</math><math>7,76</math><math>1,62</math><math>5,61</math><math>7,73</math><math>7,73</math><math>7,73</math><math>7,73</math><math>7,76</math><math>1,62</math><math>5,61</math><math>7,72</math><math>1,47</math><math>5,53</math><math>7,73</math><math>7,76</math><math>1,62</math><math>5,61</math><math>7,73</math><math>7,73</math><math>7,73</math><math>7,76</math><math>1,62</math><math>5,45</math><math>7,23</math><math>1,47</math><math>5,53</math><math>7,65</math><math>7,76</math><math>1,62</math><math>5,45</math><math>7,23</math><math>1,47</math><math>5,53</math><math>7,65</math><math>7,56</math><math>7,73</math><math>7,73</math><math>7,73</math><math>7,73</math><math>7,73</math><math>7,56</math><math>7,73</math><math>7,73</math><math>7,73</math><math>7,73</math><math>7,73</math><math>7,56</math><math>7,73</math><math>1,94</math><math>5,73</math><math>7,73</math><math>7,73</math><math>7,55</math><math>7,73</math><math>1,70</math><math>5,78</math><math>1,70</math><math>7,73</math><math>7,57</math><math>2,02</math><math>5,97</math><math>1,071</math><math>2,18</math><math>7,79</math><math>5,78</math></td><td>ExperimentExperimentRinstein's equationSelf-consistentMicromechanical<math>E'\cdot10^{-p}</math><math> X'\cdot10^{-p},  X'\cdot10^{-p},  E'\cdot10^{-p},  K'\cdot10^{-p},  K'\cdot10^{-p},</math></td><td>ExperimentRinstein's equationSelf-consistentMicromechanical theory<math>E'\cdot10^{-\bullet}</math><math>\mu'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>E'\cdot10^{-\bullet}</math><math>\mu'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>E'\cdot10^{-\bullet}</math><math>\mu'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>E'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>E'\cdot10^{-\bullet}</math><math>\mu'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>K'\cdot10^{-\bullet}</math><math>T,43</math><math>1,55</math><math>5,31</math><math>7,16</math><math>1,45</math><math>5,23</math><math>7,84</math><math>1,70</math><math>5,61</math><math>7,64</math><math>1,37</math><math>5,61</math><math>7,22</math><math>1,497</math><math>5,23</math><math>7,78</math><math>1,70</math><math>5,55</math><math>7,63</math><math>1,66</math><math>5,51</math><math>7,23</math><math>1,497</math><math>5,532</math><math>7,78</math><math>1,70</math><math>5,55</math><math>7,65</math><math>1,66</math><math>5,53</math><math>7,78</math><math>1,70</math><math>5,542</math><math>7,47</math><math>5,532</math><math>7,65</math><math>1,66</math><math>5,47</math><math>7,55</math><math>1,70</math><math>5,53</math><math>7,782</math><math>1,70</math><math>5,532</math><math>7,782</math><math>1,70</math><math>5,542</math><math>7,55</math><math>1,70</math><math>5,532</math><math>7,782</math><math>1,70</math><math>5,542</math><math>7,423</math><math>7,55</math><math>1,70</math><math>5,532</math><math>7,782</math><math>1,70</math><math>5,542</math><math>7,55</math><math>1,70</math><math>5,532</math><math>7,782</math><math>1,70</math><math>5,542</math><math>7,55</math><math>1,70</math><math>5,532</math><math>7,782</math><math>1,70</math><math>5,542</math><math>7,55</math><math>1,70</math><math>5,532</math><math>7,782</math><math>1,70</math><math>5,542</math><math>7,55</math><math>1,70</math><math>5,532</math><math>7,782</math><math>1,702</math><math>7,332</math><math>9,522</math><math>2,06</math><math>5,917</math><math>7,732</math><td< td=""><td>ExperimentExperimentEinstein's equationSelf-consistentMicromechanical theory<math>E'=14</math><math>E'\cdot10^{-9}</math><math>\mu'\cdot10^{-9}</math><math>\mu'\cdot10^{-9}</math><math>\mu'\cdot10^{-9}</math><math>\mu'\cdot10^{-9}</math><math>\mu'\cdot10^{-9}</math><math>\mu'\cdot10^{-9}</math><math>E'-10^{-9}</math><math>E'\cdot10^{-9}</math><math>\mu'\cdot10^{-9}</math><math>E'\cdot10^{-9}</math><math>\mu'\cdot10^{-9}</math><math>E'\cdot10^{-9}</math><math>\mu'\cdot10^{-9}</math><math>E'\cdot10^{-9}</math><math>E'\cdot10^{-9}</math><math>7,43</math><math>1,55</math><math>5,38</math><math>7,16</math><math>1,45</math><math>5,23</math><math>7,84</math><math>1,68</math><math>5,61</math><math>7,84</math><math>1,70</math><math>7,64</math><math>1,37</math><math>5,61</math><math>7,23</math><math>1,470</math><math>5,32</math><math>7,78</math><math>1,60</math><math>5,51</math><math>0,071</math><math>7,76</math><math>1,62</math><math>5,561</math><math>7,32</math><math>1,470</math><math>5,532</math><math>7,78</math><math>1,70</math><math>5,561</math><math>0,071</math><math>7,76</math><math>1,62</math><math>5,511</math><math>7,63</math><math>1,66</math><math>5,47</math><math>0,36</math><math>5,553</math><math>0,221</math><math>7,76</math><math>1,62</math><math>5,512</math><math>7,78</math><math>1,47</math><math>5,530</math><math>7,78</math><math>1,70</math><math>5,553</math><math>7,765</math><math>1,66</math><math>5,533</math><math>7,78</math><math>1,47</math><math>5,530</math><math>7,78</math><math>1,66</math><math>5,553</math><math>7,765</math><math>1,67</math><math>5,50</math><math>7,78</math><math>1,47</math><math>5,530</math><math>7,78</math><math>1,66</math><math>5,553</math><math>7,755</math><math>1,70</math><math>5,530</math><math>7,78</math><math>1,47</math><math>5,530</math><math>7,65</math><math>1,66</math><math>5,47</math><math>7,755</math><math>1,70</math><math>5,530</math><math>7,78</math><math>1,47</math><math>5,530</math><math>7,65</math><math>1,66</math><math>5,47</math><math>7,557</math><math>2,02</math><math>7,89</math><math>1,300</math><math>4,71</math><math>6,54</math><math>1,90</math><math>7,76</math><math>7,575</math></td><td>ExperimentEinstein's equationSelf-consistentMicromechanical theory<math>E^{-il_4,4\mu'}\psi(w)</math><math>E^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>K^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>E^{\prime,10^{-p}}</math><math>E^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>K^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>E^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>E^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}</math><math>\mu^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>\mu^{\prime,10^{-p}}</math><math>E^{\prime,10^{-p}}</math><math>7,43</math><math>1,56</math><math>5,35</math><math>7,16</math><math>1,45</math><math>5,20</math><math>7,88</math><math>1,70</math><math>5,56</math><math>0,03</math><math>7,81</math><math>1,35</math><math>5,51</math><math>7,16</math><math>1,46</math><math>5,23</math><math>7,84</math><math>1,70</math><math>5,56</math><math>0,03</math><math>7,81</math><math>1,66</math><math>5,66</math><math>7,88</math><math>1,70</math><math>5,55</math><math>0,03</math><math>0,06</math><math>7,81</math><math>1,66</math><math>5,66</math><math>7,88</math><math>1,70</math><math>5,55</math><math>0,17</math><math>7,86</math><math>5,61</math><math>7,53</math><math>1,49</math><math>5,73</math><math>1,44</math><math>5,55</math><math>0,10</math><math>7,86</math><math>5,66</math><math>7,78</math><math>1,66</math><math>5,66</math><math>7,78</math><math>0,06</math><math>7,86</math><math>5,61</math><math>7,53</math><math>1,44</math><math>5,53</math><math>7,62</math><math>0,21</math><math>0,07</math><math>7,62</math><math>5,19</math><math>8,03</math><math>1,47</math><math>5,53</math><math>7,53</math><math>1,66</math><math>5,42</math><math>0,62</math><math>7,62</math><math>5,19</math><math>8,03</math><math>1,86</math><math>5,73</math><math>7,53</math><math>1,64</math><math>5,42</math><math>0,23</math><math>7,52</math><math>2,66</math><math>5,97</math><math>10,71</math><math>2,18</math><math>7,79</math><math>5,73</math><math>1,44</math><math>5,32</math><math>0,</math></td></td<></td></tr<<>	ExperimentEinstein's equation $E' \cdot 10^{-9}$ $\mu' \cdot 10^{-9}$ , $ K' \cdot 10^{-9$	ExperimentEinstein's equationSelf- field $E' \cdot 10^{-9}$ $\mu' \cdot 10^{-9}$ $K' \cdot 10^{-9}$ $F' \cdot 10^{-9}$ $K' \cdot 10^{-9}$ $F' \cdot 10^{-9}$ $\mu' \cdot 10^{-9}$ $K' \cdot 10^{-9}$ $K' \cdot 10^{-9}$ $F' \cdot 10^{-9}$ $7, 64$ $1, 55$ $5, 35$ $7, 16$ $1, 45$ $5, 20$ $7, 88$ $7, 64$ $1, 37$ $5, 91$ $7, 23$ $1, 47$ $5, 25$ $7, 82$ $7, 81$ $1, 61$ $5, 65$ $7, 23$ $1, 47$ $5, 25$ $7, 82$ $7, 65$ $1, 63$ $5, 19$ $7, 23$ $1, 47$ $5, 23$ $7, 82$ $7, 65$ $1, 63$ $5, 19$ $7, 23$ $1, 47$ $5, 23$ $7, 23$ $7, 65$ $1, 63$ $1, 63$ $5, 25$ $7, 49$ $7, 23$ $7, 65$ $1, 63$ $1, 63$ $1, 63$ $7, 49$ $6, 49$ $7, 65$ $1, 7, 23$ $1, 63$ $1, 63$ $7, 49$ $7, 23$ $7, 65$ $1, 7, 23$ $1, 81$ $6, 49$ $6, 49$ $7, 23$ $7, 65$ $1, 7, 23$ $1, 81$ $6, 49$ $6, 49$ $7, 23$ $7, 65$ $7, 66$ $7, 68$ $1, 55$ $5, 26$ $7, 23$ $7, 88$ $7, 65$ $7, 61$ $7, 61$ $7, 23$ $1, 63$ $7, 79$ $5, 74$ $7, 65$ $7, 76$ $7, 88$ $7, 79$ $7, 79$ $5, 74$ $7, 57$ $2, 06$ $5, 97$ $10, 71$ $2, 18$ $7, 79$ $7, 57$ $2, 66$ $5, 97$ $10, 71$ $2, 18$ $7, 79$ $7,$	ExperimentEinstein's equationSelf-consiste $E' \cdot 10^{-p}$ $K' \cdot 10^{-p}$ $K' \cdot 10^{-p}$ $Field$ equation $E' \cdot 10^{-p}$ $K' \cdot 10^{-p}$ $E' \cdot 10^{-p}$ $K' \cdot 10^{-p}$ $K' \cdot 10^{-p}$ $T_{64}$ $1,55$ $5,35$ $7,16$ $1,45$ $5,20$ $7,88$ $1,70$ $7,64$ $1,37$ $5,91$ $7,23$ $1,47$ $5,25$ $7,84$ $1,66$ $7,61$ $1,65$ $7,23$ $1,47$ $5,25$ $7,76$ $1,66$ $7,61$ $1,61$ $5,65$ $7,23$ $1,47$ $5,25$ $7,76$ $1,66$ $7,62$ $1,62$ $5,61$ $7,23$ $1,47$ $5,25$ $7,76$ $1,66$ $7,62$ $1,63$ $7,23$ $1,47$ $5,25$ $7,76$ $1,47$ $7,62$ $1,63$ $5,64$ $7,63$ $1,47$ $5,58$ $7,76$ $1,63$ $5,64$ $7,69$ $1,47$ $7,57$ $2,02$ $4,87$ $8,93$ $1,56$ $5,54$ $7,79$ $1,47$ $7,57$ $2,06$ $5,97$ $10,71$ $2,18$ $7,79$ $5,78$ $1,47$ $7,57$ $2,06$ $5,97$ $10,71$ $2,18$ $7,79$ $5,78$ $1,47$ $7,57$ $2,06$ $5,97$ $10,71$ $2,18$ $7,79$ $5,78$ $1,47$ $7,57$ $2,06$ $5,97$ $10,71$ $2,18$ $7,79$ $5,78$ $1,47$ $2,56$ $5,78$ $7,79$ $5,78$ $7,79$ $1,47$ $2,66$ $5,97$ $10,71$	ExperimentEinstein's equationSelf-consistent $E' \cdot 10^{-p}$ $W' \cdot 10^{-p}$ $F' \cdot 10^{-p}$ $W' \cdot 10^{-p}$ $E' \cdot 10^{-p}$ $W' \cdot 10^{-p}$ $7.43$ $1.55$ $5.35$ $7.16$ $1.45$ $5.20$ $7.64$ $1.37$ $5.91$ $7.23$ $1.47$ $5.25$ $7.64$ $1.37$ $5.91$ $7.23$ $1.47$ $5.25$ $7.64$ $1.56$ $7.23$ $1.47$ $5.25$ $7.86$ $7.64$ $1.56$ $7.23$ $1.47$ $5.25$ $7.82$ $7.61$ $1.66$ $5.91$ $7.23$ $1.47$ $5.55$ $7.62$ $1.56$ $7.53$ $7.82$ $1.66$ $5.53$ $7.65$ $1.56$ $7.52$ $7.82$ $1.66$ $5.53$ $7.62$ $1.56$ $7.52$ $7.82$ $1.66$ $5.53$ $7.62$ $1.52$ $5.45$ $7.79$ $5.78$ $1.66$ $7.76$ $1.70$ $5.19$ $7.79$ $5.78$ $1.44$ $7.76$ $1.70$ $5.78$ $7.79$ $5.78$ $1.44$ $7.76$ $5.97$ $10.71$ $2.18$ $7.79$ $5.78$ $7.75$ $2.02$ $4.87$ $0.71$ $2.18$ $7.79$ $5.78$ $7.75$ $2.02$ $4.87$ $0.71$ $2.123$ $1.47$ $5.50$ $7.75$ $2.02$ $2.97$ $0.71$ $2.18$ $7.79$ $5.78$ $1.47$	ExperimentEinstein's equationSelf-consistentMicron $E'\cdot10^{-e}$ $\mu'\cdot10^{-e}$ $K'\cdot10^{-e}$ $\mu'\cdot10^{-e}$ $K'\cdot10^{-e}$ $K'\cdot10^{-e}$ $E'\cdot10^{-e}$ $\mu'\cdot10^{-e}$ $K'\cdot10^{-e}$ $E'\cdot10^{-e}$ $K'\cdot10^{-e}$ $K'\cdot10^{-e}$ $E'\cdot10^{-e}$ $E'\cdot10^{-e}$ $E'\cdot10^{-e}$ $E'\cdot10^{-e}$ $K'\cdot10^{-e}$ $K'\cdot10^{-e}$ $T,43$ $1,55$ $5,35$ $7,16$ $1,45$ $5,20$ $7,88$ $1,70$ $5,61$ $7,89$ $7,64$ $1,37$ $5,61$ $7,23$ $1,47$ $5,25$ $7,72$ $1,67$ $5,61$ $7,89$ $7,61$ $1,63$ $5,61$ $7,72$ $1,47$ $5,25$ $7,72$ $1,67$ $7,78$ $7,76$ $1,62$ $5,61$ $7,73$ $7,73$ $7,73$ $7,73$ $7,76$ $1,62$ $5,61$ $7,72$ $1,47$ $5,53$ $7,73$ $7,76$ $1,62$ $5,61$ $7,73$ $7,73$ $7,73$ $7,76$ $1,62$ $5,45$ $7,23$ $1,47$ $5,53$ $7,65$ $7,76$ $1,62$ $5,45$ $7,23$ $1,47$ $5,53$ $7,65$ $7,56$ $7,73$ $7,73$ $7,73$ $7,73$ $7,73$ $7,56$ $7,73$ $7,73$ $7,73$ $7,73$ $7,73$ $7,56$ $7,73$ $1,94$ $5,73$ $7,73$ $7,73$ $7,55$ $7,73$ $1,70$ $5,78$ $1,70$ $7,73$ $7,57$ $2,02$ $5,97$ $1,071$ $2,18$ $7,79$ $5,78$	ExperimentExperimentRinstein's 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TABLE	

	U, kJ/mole		60,1,81,10 60,1,81,0 60,1,81,0 60,1,81,0 60,1,81,0 60,1,81,0 60,1,81,0 60,1,81,0 60,1,81,0 60,1,81,0 60,1,81,0 60,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,81,0 7,1,1,81,0 7,1,1,81,0 7,1,1,81,0 7,1,1,81,0 7,1,1,81,0 7,1,1,1,0 7,1,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,1,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0 7,1,0,0,0 7,1,0,0,0 7,1,0,0,0 7,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,
	U2.1020,		0,73 0,73 1,257 1,
	U <sub>1</sub> ,10 <sup>20</sup> ,	ŗ	0,000 1300000000000000000000000000000000
	U'. 102",		44000044440 7,1212 1909 1001 1001 1001 1001 1001 1001
	×2.		$\begin{array}{c} 0,46\\ 0,45\\ 0,50\\ 0,52\\$
	''×	n/n	0,113 0,113 0,1150
	B,		4 4 4 4 4 4 4 4 4 4 7 3 5 0 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 5 5 5 6 4 4 4 4
	$\omega_{\rm D}^{t} \cdot 10^{-13}$ ,	łz	$\begin{smallmatrix} 0,952\\0,923\\0,999\\1,000\\1,020\\1,020\\1,020\\1,105\\1,$
	ω <sup>l</sup> <sub>D</sub> · f 0 13,		2,114 2,115 2,204 2,115 2,115 2,115 2,115 2,115 2,115 2,115 2,115 2,115 2,115 2,115 2,115 2,115 2,115 2,114 1,55 2,114 1,55 2,114 1,55 2,114 1,55 2,114 1,55 2,114 1,55 2,114 2,57 2,57 2,57 2,57 2,57 2,57 2,57 2,57
÷	e <sup>t</sup> , D,		73 77 76 76 78 76 78 78 78 78 78 78 78
	Θ <sup>ζ</sup> .		865 865 865 865 865 865 865 865 865 865
	24.	/sec	1040 1070 1070 1025 1085 1085 1120 1120 1120 1120
	'la		2310 2310 2350 2350 2390 2320 2320 2320 2320 2320 2320 232
	¢,vol.%		000 <i>0</i> 2887-0000



Fig. 2. Temperature and concentration dependence of the C<sub>V</sub> and  $\lambda$  of PVC systems. Temperature dependence of the C<sub>V</sub> of the system PVC+3%PG: 1) experiment; 2) theory. Concentration dependence of the C<sub>V</sub> of the system PVC+PG: 3) experiment; 4) theory. Concentration dependence of the  $\lambda$  of the system PVC+PG: 5) theory. C<sub>V</sub>, kJ/(Kg·K):  $\lambda$ , W/(m·K); T, K;  $\varphi$ , % by vol.

Assuming that the A and B lattices as a whole vibrate relative to each other  $(\cos(dk) = 1)$ and  $\omega_{\max}(k) = \omega_D^2$ , we obtain

$$\beta = \frac{(\omega_D^l)^2 M_A M_B}{2 (M_A + M_B)} \,. \tag{4}$$

Since the transverse vibrations are determined by the flexibility of the chain and are realized at the expense of the deformation of the valence angles, the resulting force obeys Hooke's law. In this case let the elastic constant be equal to  $\kappa$ ; then

$$\omega(k) = \left(\frac{16\varkappa}{M}\right)^{1/2} \sin^2\left(\frac{kd}{2}\right).$$
(5)

Assuming that  $\omega_{\max}(k) = \omega_{D}^{t}$ , we find

$$\varkappa = \frac{(\omega_{\rm D}^{t})^2 M}{16} .$$
 (6)

Calculating in accordance with equations (4) and (6), we obtain the dependence of the quasielastic constants on the loading of the PVC with the filler PG. An analysis of the dependence of  $\beta$  on  $\varphi$  shows that on the filler concentration range 3-5% by vol. the values of  $\beta$ are observed to decrease, while on an interval of the order of 20% by vol. they increase sharply. It should be noted that over the entire filler concentration range the constant of quasi-elastic interaction between CH<sub>2</sub>-CHCl groups is higher than for the initial PVC. A comparison of the quasi-elastic constants of transverse interaction of the structural units of the system shows that in the case of interaction of the types H-H( $\varkappa_1$ ) and H-Cl( $\varkappa_2$ ) the value  $\varkappa_1 < \varkappa_2$ , and on the filler concentration interval 0.3-20.0% by vol.  $\varkappa_2$  is observed to increase, especially on the range 5-20%. The constant  $\varkappa_1$  varies only slightly. Consequently, the introduction of filler in amounts of the order of 1.0% by vol. or more leads to a strengthening of the crosslinks in the system.

Analyzing the temperature dependence of  $\beta$ , $\varkappa_1$ , and  $\varkappa_2$ , we conclude that an increase in the temperature of the PVC composition leads to a decrease in the values of the quasi-elastic interaction constants and hence to a decrease in the interaction between the structural elements of the system.

Considering that the interaction between the atoms along the main chain of the macromolecule is equal to  $F = \beta x$ , the energy of the quasi-elastic component in the longitudinal direction will be equal to U' =  $\beta x^2/2$  and in the transverse direction to  $U_1 = \varkappa_1 x_1^2/2$  and

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Temperature Depen	rature Depen	Depen	qe	nce of 1	the Vis	coelast	tic and	Thermo	physica	1 Prope	rties c	f the 1	System	PVC+3%PG
Ω <sub>1</sub> Φ <sup>1</sup> Φ <sup>1</sup> Φ <sup>1</sup> Φ <sup>1</sup> Φ <sup>1</sup> Φ <sup>1</sup>	α <sup>Γ</sup> <sub>10-12</sub> , α <sup>Γ</sup> <sub>10-12</sub> , α <sup>Γ</sup> <sub>10-12</sub> ,	ω <sup>2</sup> .10-13, Φ <sup>2</sup> .10-13,	ο <sup>Φ</sup> . 10-13,	$\theta_{D}^{l}$		D, O O	e	X4 ,	Xz,	U'. 1020	U1.1020,	U2.10 <sup>20</sup> ,	Uo.102 <sup>0</sup> ,	U, kJ/mole
m/sec Hz	/sec Hz	Hz	Iz		~	Y		N/m			-7			
2320 1120 2,115 1,020 162	1120 2,115 1,020 162	2,115 1,020 162	1,020 162	162		78	4,04	0,15	0,52	4,79	0,09	0,82	1,213	47,1
2250 1100 2,053 1,004 157	1100 2,053 1,004 157	2,053 1,004 157	1,004 157	157		77	3,81	0,15	0,51	4,52	0,09	0,81	1,234	45,5
2190 1080 1,999 0,986 153	1080 1,999 0,986 153	1,999 0,986 153	0,986 153	153		75	3,61	0,14	0, 49	4,28	0,08	0,78	1,254	43,7
2120 1050 1,935 0,958 148	1050 1,935 0,958 148	1,935 0,958 148	0,958 148	148		73	3,38	0,13	0,46	4,01	0,08	0,73	1,275	41,6
2060 1030 1,880 0,940 144	1030 1,880 0,940 144	1,880 0,940 144	0,940 144	144		72	3,19	0,13	0,44	3,78	0,08	0,70	1,296	40,0
2000 1020 1,825 0,931 140	1020 1,825 0,931 140	1,825 0,931 140	0,931 140	140		12	3,01	0,13	0,44	3,57	0,08	0,70	1,317	38,8
1910         1010         1,743         0,922         133	1010 1,743 0,922 133	1,743 0,922 133	0,922 133	133		70	2,74	0,12	0,43	3,25	0,07	0,68	1,337	36,7
1830 995 1,670 0,908 128	995 1,670 0,908 128	1,670 0,908 128	0,908 128	128		69	2,52	0,12	0,41	2,99	0,07	0,65	1,358	34,9
1800         970         1,643         0,885         126	970 1,643 0,885 126	1,643 0,885 126	0,885 126	126		68	2,44	0,11	0,39	2,89	0,06	0,62	1,379	33,7
1740         940         1,588         0,858         121	940 1,588 0,858 121	1,588 0,858 121	0,858 121	121		66	2,28	0,11	0,37	2,70	0,06	0,59	1,400	32,5
1680         920         1,533         0,840         117	920 1,533 0,840 117	1,533 0,840 117	0,840 117	117		64	2,12	0,10	0,35	2,51	0,06	0,55	1,420	31,0
1610         900         1,468         0,821         112	900 1,468 0,821 112	1,468 0,821 112	0,821 112	112		63	1,95	0,10	0,34	2,31	0,06	0,54	1,441	29,8
1570         860         1,432         0,785         109	860 1,432 0,785 109	1,432 0,785 109	0,785 109	109		09	1,85	0,09	0,31	2,19	0,05	0,49	1,461	28,5
1530         810         1,396         0,739         107	810 1,396 0,739 107	1,396 0,739 107	0,739 107	107		56	1,76	0,08	0, 27	2,09	0,05	0,43	1,482	27,3

 $U_2 = \frac{1}{2} x_2^2/2$ . Assuming that  $x \approx d$ , where d is the interatomic spacing, which is equal to 1.54 Å for C-C and 1.08 and 1.78 Å for H-H and H-Cl respectively, we determine U',  $U_1$ , and  $U_2$ . As the calculations show, the interaction energy  $U_1$  is unimportant as compared with U' and  $U_2$  (U'/ $U_1 \approx 50$ ;  $U_2/U_1 \approx 10$ ). Taking into account the thermal motion of the structural elements, we find its energy as  $U_0 = i/2$  kT. Then the total energy of the interacting structural elements is equal to

$$U = U_0 + U' + U_1 + U_2 = \frac{i}{2}kT + \frac{\beta x^2}{2} + \frac{\varkappa_1 x_1^2}{2} + \frac{\varkappa_2 x_2^2}{2}.$$
 (7)

The results obtained (Tables 2 and 3) show that the interaction energy of the system depends on the PG concentration and temperature. At a filler content of 1-2% by vol. U has a maximum, and on the interval  $\varphi \ge 10\%$  by vol. is observed to grow strongly. An analysis of the temperature dependence shows that as the temperature rises, the interaction energy decreases, and its temperature dependence can be controlled by means of the PG content.

Starting from the data on the propagation velocity of an ultrasonic wave in the system, we will determine the thermophysical properties of the PVC composition.

For this purpose we divide the spectral distribution density into two components [5]:

$$\rho(\omega) = \rho_l(\omega) + 2\rho_t(\omega), \tag{8}$$

where

$$\rho_l = \frac{V}{2\pi^2 v_l^3} \ \omega^2 \text{and} \ \rho_t = \frac{V}{2\pi^2 v_t^3} \ \omega^2,$$

and normalize each part on N:

$$\int_{0}^{\omega_{\mathrm{D}}^{l}} \rho_{l}(\omega) \, d\omega = N, \quad \int_{0}^{\omega_{\mathrm{D}}^{l}} \rho_{t}(\omega) \, d\omega = N.$$

Then the specific heat  $(C_V)$  can be determined as

$$C_{V} = Nk D\left(\frac{-\Theta_{D}^{l}}{T}\right) + 2Nk D\left(\frac{-\Theta_{D}^{t}}{T}\right), \qquad (9)$$

where

$$\Theta_{\rm D}^{l} = -\frac{\hbar \, (6\pi^2 N)^{1/3} \, v_l}{k V^{1/3}} \, ; \, \Theta_{\rm D}^{t} = -\frac{\hbar \, (6\pi^2 N)^{1/3} \, v_t}{k V^{1/3}}$$

are the characteristic Debye temperatures.

The calculations show that as the temperature rises, the  $\Theta_D^L$  and  $\Theta_D^L$  of the PVC systems tend to decrease. Typically, over the entire temperature range investigated  $\Theta_D^L < \Theta_D^L$ . Furthermore, it should be noted that  $\Theta_D^L$  and  $\Theta_D^L$  are also functions of the filler concentration in the system. On the range 10-2% by vol. PG the quantities  $\Theta_D^L$  and  $\Theta_D^L$  vary by 18 and 23 K respectively.

As follows from the data presented in Fig. 2, on the interval 290-370 K the C<sub>V</sub> values of the PVC systems calculated from relation (9) are close to the experimental values. The C<sub>V</sub> of the system varies only slightly as the filler concentration increases on the interval investigated. This also finds confirmation in the experimental dependence of C<sub>V</sub> on  $\varphi$ .

We will calculate the thermal conductivity of the poler system taking into account the fact that the structure of an amorphous polymer is a set of subsystems of constantly increasing complexity, statistically distributed in the system relative to the heat flux, energy being exchanged between them by contact heat conduction. We assume that the heat transfer is associated with the transfer of energy along the main valence chain of the micromolecule by longitudinal phonons, with velocity  $v_{\ell}$ , and by energy exchange between side-chain atoms or groups of atoms and between neighboring macromolecules attributable to transverse phonons with velocity  $v_t$  [11, 12]. We assume that the polymer matrix is homogeneous and isotropic, that there are no internal heat sources, and that the time of action of the temperature field on the system investigated t  $\ll \tau_i$ , where  $\tau_i$  is the finite lifetime of the structures investigated; then the effective thermal conductivity coefficient of the structural subsystem can be determined in accordance with the heat balance equation

$$C_V \rho V = \frac{2 \sqrt{\lambda_l C_V \rho}}{\sqrt{\pi}} \sqrt{\tau} S, \qquad (10)$$

where S is the cross section of the subsystem, and  $\tau$  is the time taken by the system to reach equilibrium temperature. Solving equation (10) and using the rules of transition from subsystem to system [13], we obtain

$$\lambda_l = -\frac{\pi}{12} C_V \rho v_l l, \tag{11}$$

where  $\ell$  is the mean free path for longitudinal phonons. Considering that in the propagation of thermal energy each structural subsystem is characterized by the dissipative energy losses  $(Q_t)$  associated with the side groups or branches of the macromolecules, we determine the thermal conductivity in this direction  $(\lambda_t)$  as [12]:

$$\lambda_t = \frac{\rho v_t C_V a}{8} , \qquad (12)$$

where a is the effective cross section of the subsystem.

On the basis of relations (11) and (12), the thermal conductivity coefficient of flexiblechain amorphous polymers and their systems will be:

$$\lambda = C_V \rho \left( \frac{\pi}{12} v_l l + \frac{a v_t}{8} \right). \tag{13}$$

An analysis of the results obtained shows that the calculated values of the thermal conductivity and the experimental data are in satisfactory agreement. Only on the filler concentration interval 5-20% by vol. is the value of  $\lambda$  observed to increase (Fig. 2).

The properties of PVC can be controlled by using waste from phosphoric acid and (or) mineral fertilizer production in the form of high-dispersity phospho-gypsum.

## NOTATION

 $v_{\ell}$  and  $v_t$  are the longitudinal and shear strain rates;  $\omega$  is the investigation frequency;  $\rho$  is the density;  $\alpha_{\ell}$  and  $\alpha_t$  are the longitudinal and shear wave absorption coefficients; E',  $\mu$ ', and K' are the real parts of the longitudinal, shear, and compression moduli;  $\omega_D^{\ell}$  and  $\omega_D^{t}$ are the characteristic Debye frequencies for the longitudinal and shear waves; U is the total energy of the interacting elements;  $\rho(\omega)$  is the spectral distribution density;  $D\left(\frac{\Theta_D^l}{T}\right)$  and  $D\left(\frac{\Theta_D^l}{T}\right)$  are Debye functions; C<sub>V</sub> is the specific heat; and  $\lambda$  is the thermal conductivity co-

efficient.

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DAMPING OF THE MECHANICAL VIBRATIONS OF A PIEZOELECTRIC ELEMENT BY SENSITIVE COATINGS

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A method of calculating the viscoelastic properties of moisture-sensitive polymer films deposited on the piezoelectric element of a quartz resonator is proposed.

In quartz atmospheric humidity sensors that employ the energy measuring principle the role of moisture-sensitive element is played by thin polymer films deposited on the piezoelectric element of the quartz resonator [1, 2]. The change in the damping properties of the polymer film as a result of the sorption of water vapor from the air leads to a change in the dissipation of the mechanical energy of the quartz resonator and its equivalent electrical resistance. Sensors of this kind have been called dissipative quartz mechanical energy transducers (DQMET).

The sensitivity of DQMET to a nonelectric quantity such as atmospheric humidity depends on the damping capacity of the sensitive coatings deposited on the piezoelectric element of the quartz resonator and its dependence on the parameter being monitored. The output parameter of the DQMET is its equivalent resistance R [3]:

$$R = K_0 \eta_{\mathbf{f}} \Delta_{\mathbf{f}},\tag{1}$$

where  $K_0$  is the conversion coefficient of the piezoelectric element, ohm sec/kg, and  $\eta_f$  and  $\Delta_f$  are the viscosity, Pa sec, and thickness, m, of the sensitive film.

The viscosity of the film (internal friction) varies with the parameter monitored, for example the humidity of the air, affecting the dissipation of the elastic vibration energy of the piezoelectric element and causing a corresponding change in the equivalent resistance of the quartz resonator. If the viscosity of the sensitive polymer is too great, there will be a decrease in its damping capacity expressed in a decrease in the equivalent resistance of the DQMET with increase in viscosity, which limits the range of application of expression (1). In our opinion, this effect is attributable to relaxation processes in the polymer film.

For DQMET intended to serve as atmospheric humidity sensors it is proposed to use a polyamide (Kapron, nylon-6) coating [2]. We will consider the variation of the damping properties of a polyamide filament with relative humidity when vibrations are excited in the filament at a frequency of 100 Hz. Figure 1 shows the loss modulus E" =  $\omega\eta$  and the modulus of elasticity E' of the filament as functions of the relative humidity  $\phi$  [4]. The loss modulus has a maximum at 60% relative humidity. With further increase in humidity the loss modulus decreases. We will explain this effect from the standpoint of relaxation theory.

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