Thermodynamic compatibility and structural characteristics of interpenetrating polymer vibration damping systems for engineering purposes

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Abstract. This article is devoted to the study of thermodynamic compatibility and structural characteristics of interpenetrating polymer systems (IPS) based on thermosetting and thermoplastic polymers for the production of vibration-damping and sound-absorbing composite polymer materials for machine-building purposes. IPS based on epoxy polymer and polyurethane is calculated according to the well-known Flory-Scott theory at a temperature of 373 K to obtain thermodynamic compatibility of the components of the mixture. Studies have established that between the macromolecules of homopolymers that make up the system, a donor-acceptor mechanism of covalent bonding occurs due to an unshared electron of the nitrogen atom and a cross-linked structure of interpenetrating polymer systems is formed, due to the thermodynamic compatibility of the components. The studies determined that at a temperature of 330 K, the coefficient of mechanical losses has a maximum corresponding to the relaxation process associated with the segmental mobility of the chain and the dynamic modulus of elasticity of the composition monotonically decreases with increasing temperature. The maximum vibration-absorbing properties based on epoxy and polyurethane polymers can be obtained at their ratio of 65:35.

1 Introduction

As it is known, today a large number of vibration-absorbing viscoelastic composite polymer materials and coatings based on them are being developed and widely used for use in mechanical engineering and other industries [1-9].

A special place in the research of the properties of vibration-damping-viscoelastic materials is occupied by works devoted to IPS [10-14].

The creation of a IPS opens up wide possibilities for modifying the properties of mesh and linear polymers, which is an important issue. The use of polymers of various structures for the production of IPS is promising because the combination of various systems or grids

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with linear macromolecules is possible on the basis of existing large-tonnage raw materials and to solve many fundamentally new technical problems [10, 15].

An ideal IPS is a system in which the interpenetration of heterogeneous chains is carried out at the molecular level. Partially interpenetrating polymer systems are the result of incomplete mixing of components and are characterized by one wide maximum of mechanical losses at the glass transition temperature [2, 3, 10, 15, 16].

IPS based on incompatible polymers are distinguished by a clear separation of the maximum mechanical losses that make up the system of components. In this case, the glass transition temperatures of homopolymers in the IPS must meet the requirements for individual grids. Obtaining such chains is also unlikely [2].

When developing multicomponent systems, first of all, the question arises about the thermodynamic compatibility of the constituent components [17].

The aim of the study is to study the thermodynamic compatibility and structural characteristics of interpenetrating polymer systems and the development of vibration-damping composite polymer materials for use in mechanical engineering.

2 Objects and methods of research

The objects of the study are IPS based on epoxy resins ED-16, ED-20 (State standard 10587-76), alkylresorcinol epoxy resin EIS-1 (TC38-103-76), dibutylphtholate-DBP, polyethylene polyamine-PEPA, thermoplastic polyurethane and thermoelastoplast grade PR (TC 38-103-185-92).

A vibration damping-viscoelastic property was determined on an experimental setup (TC02-123-92) by determining the mechanical losses of the polymer or interpenetrating systems [17].

$$\eta = \frac{\omega_1 - \omega_2}{\sqrt{\lambda^2 - 1}\ \omega p}$$

where, ω_p is the resonant frequency, Hz; ω_2 is the frequency of vibrations in the resonant region at the level of the disturbing force P_{min}, ω_1 is the frequency of vibrations in the resonant region at the level of the disturbing force P_{min}, equal to λ R_{min}, Hz; λ is the level of the disturbing force P_{min}, at which ω is determined before and beyond the resonant regions.

3 Results and their discussion

When studying the vibration damping-viscoelastic properties of two component systems, including interpenetrating polymer systems, first of all, the question arises about the thermodynamic compatibility of the components [9, 10].

The thermodynamic criterion for the compatibility of polymers in mixtures is a negative value of the Gibbs free mixing energy (ΔG) or the enthalpy of polymer mixing. The value of the Gibbs free mixing energy of IPS based on ED-16 + PU, ED-20 + PU and EIS-1 + PU were calculated according to the well-known theory of thermodynamic compatibility of polymer melts of the Flory-Scott theory at a temperature of 373 K [18].

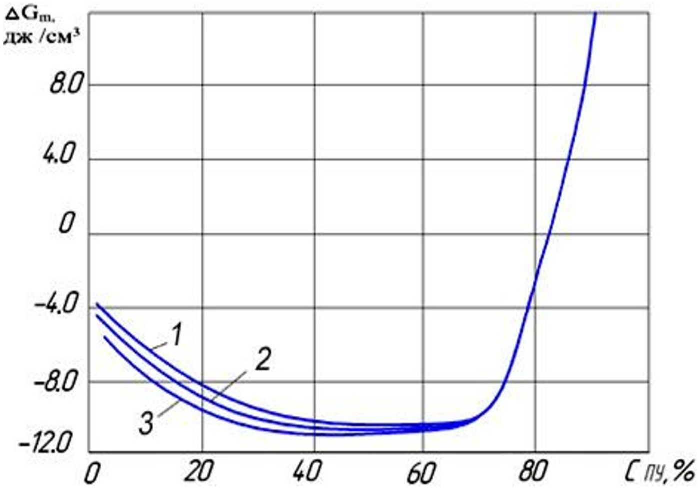
The calculation results are shown in Table 1 on the example of the ED-16 + PU system. It can be seen (Table.1) that in the range of ED-16: PU ratios from 80:20 to 30:70, the Gibbs mixing energy has a negative value. This shows that in this ratio range, thermoplastic polyurethane dissolves in the epoxy oligomer ED-16.

Table 1. Thermodynamic compatibility of the components of the mixture ED-16 + PU

Composition of IPS (in volume, fractions, %)		Gibbs free mixing energy ΔG, J/cm
ED-16	PU	
90	10	+0.026
80	20	-0.416
70	30	-0.694
60	40	-0.823
50	50	-0.800
40	60	-0.610
30	70	-0.225
20	80	+0.408

Further, the thermodynamic compatibility of the epoxy oligomer-polyurethane-maleic anhydride (MA) system was studied. The latter is a common solvent for both components of the system.

The thermodynamic compatibility of this three-component system was also calculated according to the Flory-Scott theory for the case in the presence of a common solvent in the system. Unlike the epoxy oligomer - polyurethane system in the ED-16+PU+MA, ED-20 + PU+MA and EIS-1+PU+MA. The thermodynamic compatibility of the components is manifested up to the polyurethane content in the system up to 77% (Fig. 1).



1 – ED-16; 2 – EIS-1; 3 – ED-20

Fig. 1. Dependence of the Gibbs free mixing energy on the polyurethane content in the mixture

It can be seen (Fig. 1) that the molecular weight of oligomers has a significant impact on the compatibility of system components. With an increase in the molecular weight of the oligomers, the Gibbs mixing energy decreases several times to a certain value (with a polyurethane content of up to 70%), in which the system will be compatible, and then with a further increase in the molecular weight of the oligomer, the Gibbs free mixing energy increases and tends to positive values, that is, the system will be incompatible.

The study of the thermodynamic compatibility of the above polymer pairs made it possible to determine the ratio interval of the components to be studied.

In order to clarify the possibility of the formation of a chemical bond between the macromolecules of homopolymers that make up the system, infrared spectra of homopolymers and IPS based on them were obtained, where the ratio of components was equal. ED: PU 75:25.

In the IR spectrum of the cured epoxy oligomer ED-16 with maleic anhydride (Fig. 2), there were: a low-intensity band at 2970 cm^{-1} from valence vibrations of C-C bonds in CH-CH groups in the aromatic ring; bands at 1710, 1600, 1500 cm^{-1} from valence vibrations of C = O, C =C, C-CH bonds in the structure of the anhydride ring, the benzene ring and the structure of the aromatic ring; the band at 1230 cm^{-1} from the deformation vibration of C=O bonds: a low-intensity absorption band at 1030 cm^{-1} from the deformation vibrations of C-O-C bonds and a band at 830 cm^{-1} from out-of-plane vibrations of CH-bonds, substituted benzene ring and vibrations of the structure of C-(CH) bonds.

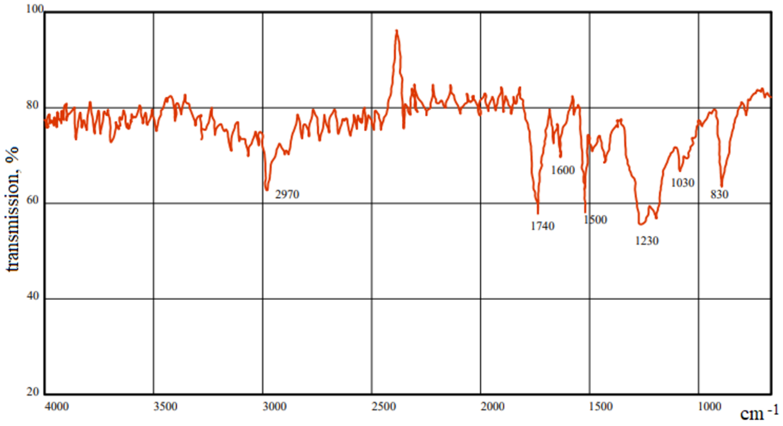


Fig. 2. IR spectra of ED-16 epoxy oligomer cured with maleic anhydride

In the IR spectra of polyurethane (Fig. 3) there are: an intense band at 3350 cm^{-1} from valence vibrations of amide groups = NH bonds, a band at 2950 cm^{-1} from valence vibrations of C-C bonds in methyl groups; intense bands at 1730, 1600 and 1530 cm^{-1} from valence vibrations of C =O, C=C, C=CH bonds in the urethane group and benzene ring; bands at 1460, 1410 cm^{-1} from deformation vibrations of C =C bonds in the aromatic ring; intense band at 1370 cm^{-1} from deformation vibrations of hydroxyl groups; wide intense bands at 1250 and 1150 cm^{-1} from deformation vibrations of C-O-C complex ether bonds; an intense band at 950 cm^{-1} from vibrations of CH-bonds; and bands at 770 and 730 cm^{-1} from out-of-plane vibrations of CH-CH bonds of the substituted benzene ring.

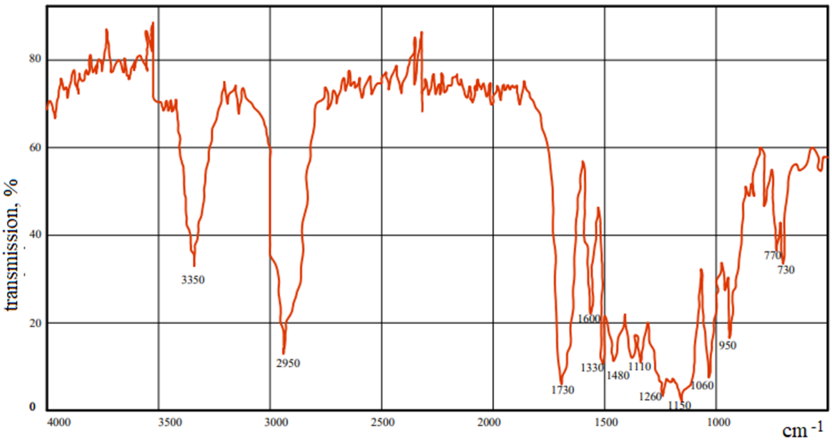


Fig. 3. IR spectra of polyurethane

Let's consider the IR spectra of the IPS based on the epoxy oligomer ED-16, cured with maleic anhydride and polyurethane grade UK-1. It can be seen from the obtained spectra (Fig. 4) that the absorption bands of bonds in the functional groups of homopolymers are completely repeated with some of their displacements. At the same time, the intensity of the absorption bands is significantly reduced.

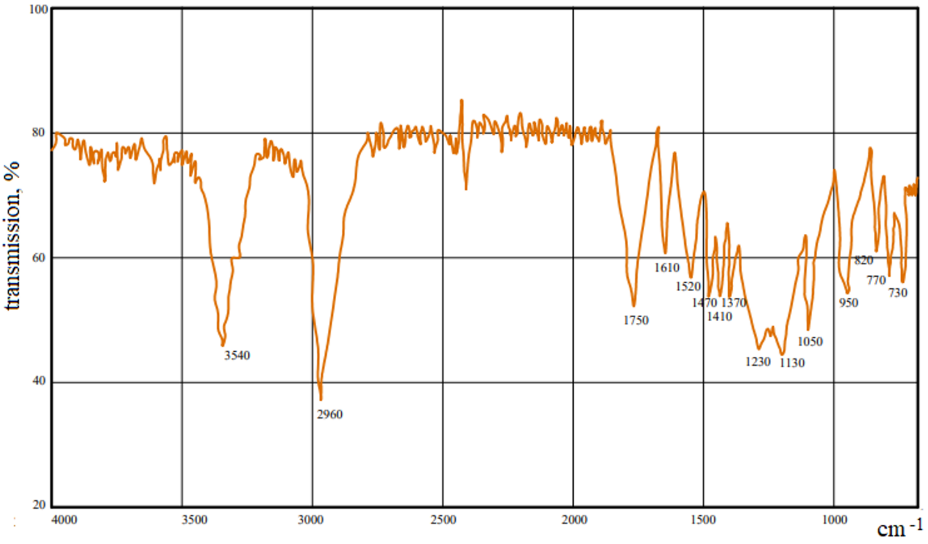
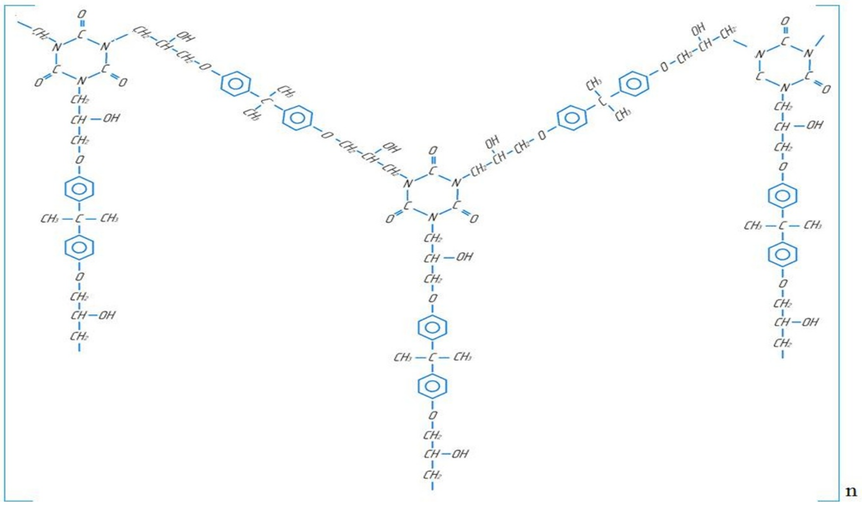


Fig. 4. IR spectra of IPS based on ED-16 and polyurethane UK-1 (ED:PU 75:25)

The proposed mechanism of interaction of the ED-16 epoxy oligomer with polyurethane is given below:



As can be seen from the interaction mechanism, oligomers bind to each other by a covalent bond, forming IPS. Thus, in the IR spectra of the studied IPS, the intensity of the absorption bands decreases significantly, which allows us to conclude that a donor-acceptor

https://doi.org/10.1051/e3sconf/202340105095

mechanism of covalent bonding occurs between the macromolecules of the homopolymers that make up the system due to the unshared electron of the nitrogen atom and a cross-linked structure of interpenetrating polymer systems is formed.

X-ray diffractograms of homopolymers and interpenetrating IPS systems based on them were studied. On an X-ray diffractogram of an epoxy polymer, at an X-ray sliding angle equal to 22A °, only one maximum corresponding to an amorphous polymer is observed (Fig. 5).

Analysis of the X-ray diffraction pattern of thermoplastic polyurethane UK-1 showed that the structure of the linear polymer consists of crystalline and amorphous regions (Fig. 6). The mass degree of crystallinity of polyurethane reaches up to 20%. At the same time, four crystallinity regions with different interplane distances are observed, equal to 3.68 A° at 28 A°, 3.97 A° at 26 A°, 4.10 A° at 25 A° 30’ and 5.0 A° at 20 A° 45'.

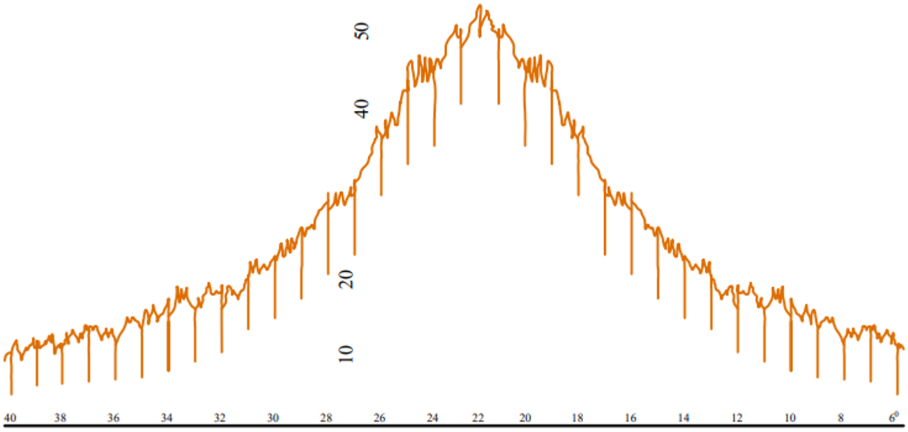


Fig. 5. X-ray diffractogram of epoxy oligomer cured with maleic anhydride

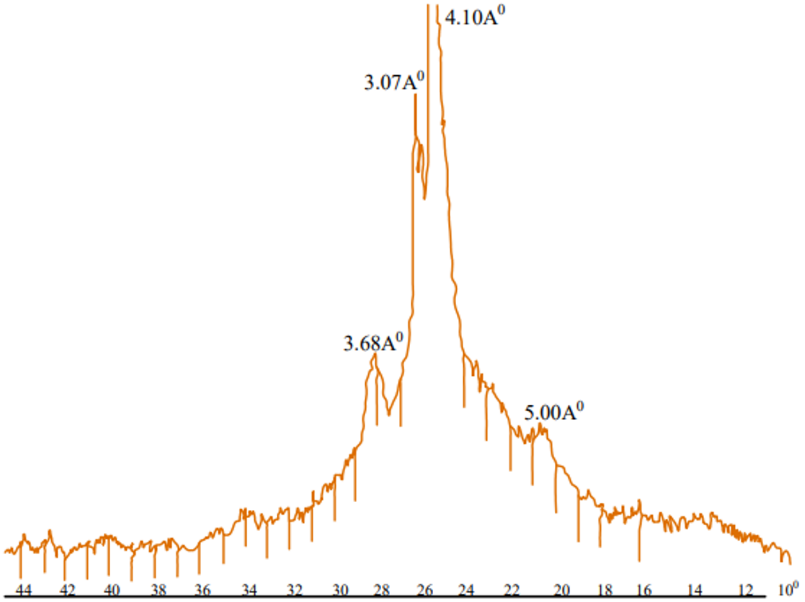


Fig. 6. X-ray diffractogram of polyurethane UK-1

In X-ray diffractograms of the VPS based on the above components - the ED-16 oligomer and polyurethane, up to a component ratio equal to 50:50 (Fig. 7), crystalline regions of the thermoplastic polymer are not observed, the entire structure of the mixture consists of amorphous regions. The spherulite supramolecular structure of polyurethane is destroyed and passes into fibrils and lamellae. These changes in the structure of polyurethane give reason to believe that mutual penetration in this IPS is carried out at the supramolecular level.

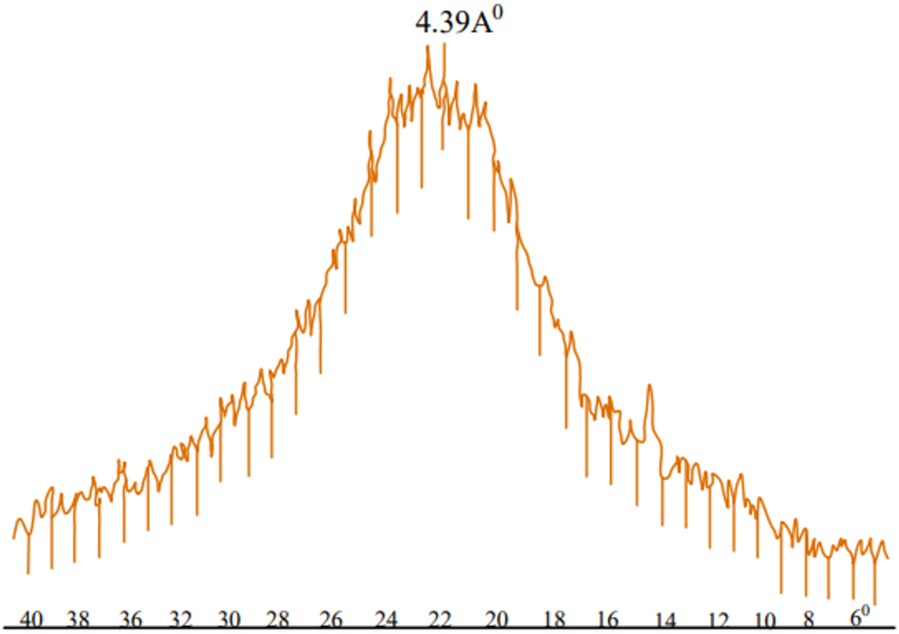


Fig. 7. X-ray diffractogram of interpenetrating systems - IPS (ED: PU 50:50)

In the IPS, where the dispersed medium is polyurethane and the phase is an epoxy polymer, in the X-ray diffraction pattern (Fig. 8), the crystalline regions in the thermoplastic polymer reappear with increasing temperature. This is apparently due to the fact that the resulting mesh structure of the epoxy polymer is insufficient to provide resistance, in which the formation of crystalline regions in polyurethane occurs. The results obtained indicate the development of significant heterogeneity in the IPS and confirm the conclusions that the IPS cannot be considered as a homogeneous two-phase system with a uniform distribution of phases in the volume of the mixture.

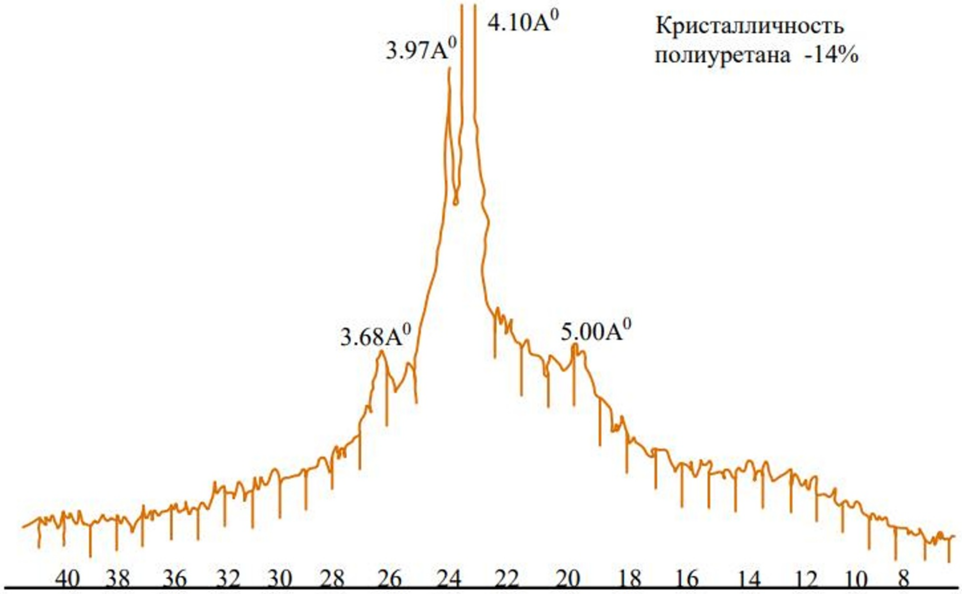


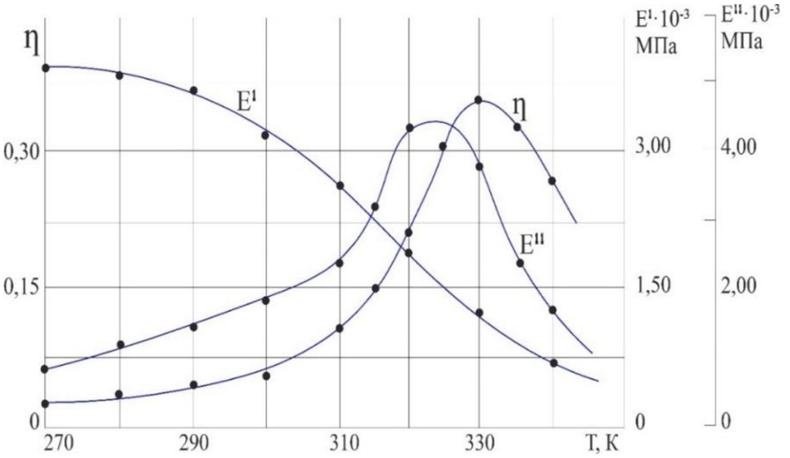
Fig. 8. X-ray diffractogram of interpenetrating systems-IPS (ED: PU 30:70)

The reason for this, as noted above, is the thermodynamic incompatibility of the components, which leads to the stratification of the constituent phases occurring during the formation of the IPS. Due to the slow kinetics of phase separation during the formation of the IPS, due to the high viscosity of the polymer system, complete phase separation does not occur, as a result, a transition region is formed.

Thus, with the help of radiography, it was found that transition regions are formed in the IPS, due to the spherulitic supramolecular structure of the components.

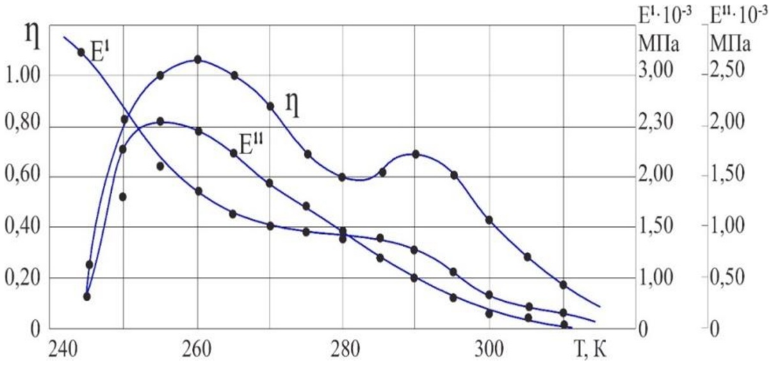
Next, we investigated the viscoelastic properties of epoxy polymer and polyurethane. The viscoelastic properties of an epoxy composition based on an ED-16 oligomer, a DBP plasticizer and a PEPA hardener were studied depending on temperature (Fig. 9). DBP was introduced into the composition in order to reduce internal stresses in a thermosetting polymer [19, 20, 21].

9 shows that at a temperature of 330 K, the mechanical loss coefficient has a maximum corresponding to the relaxation process associated with the segmental mobility of the chain. The dynamic modulus of elasticity of the composition monotonically decreases with increasing temperature. If we take into account that the glass transition temperature of an epoxy polymer without DBP is 355-360 K, then DBP in the amount of 25 mass parts reduces the glass transition temperature of the composition by 25-30 K. At the same time, the value of the mechanical loss coefficient decreases from 0.58 to 0.36 at the corresponding glass transition temperatures. The width of the maximum increases significantly due to the increased flexibility of the circuit in the presence of the DBP composition. A further increase in the DBP content is impractical, since its compatibility limit of ED-16 is up to 25 mass parts.



Composition: ED-16 – 100 m.p., DBP – 25 m.p., and PEPA - 10 m.p.
Fig. 9. Temperature dependence of the damping-viscoelastic properties of the epoxy composition

Experimental studies of viscoelastic properties of thermo-plastic polyurethane UK-1 have shown (Fig. 10) that it has a high coefficient of mechanical losses n in the glass transition temperature region, but a relatively low modulus of elasticity at normal temperature.



Composition: ED-16 – 100 m.p., DBP – 25 m.p., and PEPA - 10 m.p.
Fig. 10. Temperature dependence of damping-viscoelastic properties of polyurethane UK-1

Such high values of the coefficient of mechanical losses (n-1.08) are due to the presence of various functional groups (urethane, urea, allophanate) in the structure of polyurethane. At a temperature of 260 K, segmental mobility of the chain of polyurethane macromolecules responsible for the relaxation process is observed, and the relaxation process taking place at a temperature of 290 K is associated with the mobility of individual polymer macromolecules in crystalline regions.

The study of the influence of the ratio of crosslinking agents of polyurethane on its properties showed that an increase in low molecular weight diol (1.4 BD) leads to a decrease in the coefficient of mechanical losses due to an increase in the proportion of rigid blocks in the system, and the modulus of elasticity of polyurethane increases.

Thus, it was revealed that the epoxy polymer from the ED-16 oligomer, cured by PEPA, has a relatively low coefficient of mechanical losses, but a high modulus of elasticity E'. Polyurethane, on the contrary, has a high value of the coefficient of mechanical losses, but a moderate modulus of elasticity at normal temperature. Therefore, it can be expected that a mixture based on these homopolymers should have high viscoelastic properties.

The study found that the characterized product of the maximum values of the elastic modulus and the absorption coefficient of interpenetrating systems based on epoxy polymers and polyurethane is established with their ratios equal to 65:35.

4 Conclusions

Thermodynamic and structural characteristics of interpenetrating systems – IPS based on epoxy polymers and polyurethane were investigated. The calculation of the thermodynamic compatibility of this three-component system was carried out according to the theory of Flora-Cattle for the case in the presence of total dissolution in the system. The study of the thermodynamic compatibility of these polymer pairs made it possible to determine the ratio interval of the components to be studied.

IR spectroscopic examination has established that a polycondensation reaction occurs between polymer macromolecules and covalent bonds form between the molecules, which substantiate the existence of interpenetrating polymer systems.

It is revealed that the thermodynamic incompatibility of the components, which leads to the stratification of the constituent phases occurring during the formation of the IPS, depends on the supramolecular structure of the composition. Due to the slow kinetics of phase separation during the formation of the IPS, due to the high viscosity of the polymer system, complete phase separation does not occur, as a result of this, a transition region of the system from an amorphous state to a crystalline one is formed.

The limit of compatibility of the ED-16 oligomer with the plasticizer dibutylphtholate up to 25 mass parts has been established, which allows reducing internal stresses in coatings and improving mechanical properties. At a temperature of 330 K, the coefficient of mechanical losses has a maximum corresponding to the relaxation process associated with the segmental mobility of the chain, and the modulus of dynamic elasticity of the composition monotonically decreases.

The study shows that the viscoelastic property of thermoplastic polyurethane UK-1 has a high coefficient of mechanical losses in the glass transition temperature region, but a relatively low modulus of elasticity at normal temperature.

Therefore, it can be noted that the epoxy oligomer from ED-16, cured with a polyethylene polyamine – PEPA hardener, has a relatively low coefficient of mechanical losses, but a high modulus of elasticity E'. Polyurethane, on the contrary, has a high value of the coefficient of mechanical losses, but a moderate modulus of elasticity at normal temperature.

Thus, it can be expected that the mixture-composition based on these homopolymers should have high viscoelastic damping characteristics. It has been established that in the ED-PU system, with composition ratios of 65:35, the coefficient of mechanical losses is within the high limits of 1.27, the use of which allows to increase the efficiency and durability in conditions of vibration of parts, thin-walled structures, working bodies of machines and mechanisms, as well as to reduce noise and improve working conditions in industrial premises.

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