

*Chapter 1*

## **POLYMER/SILICATE NANOCOMPOSITES BASED ON ORGANOMODIFIED CLAYS**

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### **ABSTRACT**

It should be known that a lot of studies devoted to the preparation of polymer nanocomposite materials have been investigated at recent years. The amount of such works increases intensively. The possibility of preparation such materials was shown for practically all kinds of polymerized and polycondensed polymer materials. Investigators demonstrate particular interest to the organomodified montmorillonite as an element of nanotechnology and bearer of nanostructure with great difference between its length and thickness. In this case the organomodification is carried out by using of ionic surfactants. The using of nonionic surfactants for hydrophobization of clay's surface also found reflection in some works. Common steady understanding is formed about investigation technique and structure of polymer nanocomposite materials and how thermo-mechanical properties depend on its structure. The increasing in amount of such investigations shows that this perspective technology will find reflection in industrial application.

**Keywords:** nanocomposite, organoclay, fire retardant polymer.

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During last years one of the most perspective fields of polymer science there is a preparation of polymer materials that have a lot of improved and new properties. Such properties can be attributed to the new kind of materials calling polymer nanocomposites that can be used in different branches of polymer applications.

To achieve improved properties in polymer composites have to use such additives as pigments, inhibitors, antioxidants, plasticizers and other compounds. Materials including the inorganic particles (oxides, nitrides, carbides, silicates etc.) are introduced to the polymer matrix in case of nanocomposites. Main our interest devoted to the polymer nanocomposite materials based on organomodified layered silicates [1]. Incompatibility of these inorganic and organic components – main problem has to be solved. There is method to overcome this problem. It's a modification of clays by organic ionic or nonionic compounds. Modified clay (organoclay) has some advantages in comparison with simple clay:

- 1) Organoclays can be well dispersed in polymer matrix [2].
- 2) Organoclays interacted with polymer's chain [3].

For preparation of such nanocomposites based on organoclays have to be used layered natural inorganic structures as montmorillonite [4, 5, 6], hectorite [3], vermiculite [7], saponin [8], kaolin, etc. Length of these layers about 220 nm, and thickness – 1 nm [9, 10].

Their crystal structure consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either alumina or magnesia. Stacking of the layers leads to a regular Van der Waals gap between the layers, called the *interlayer* or *gallery*. Isomorphous substitution of  $\text{Si}^{4+}$  for  $\text{Al}^{3+}$  in the tetrahedral lattice, and of  $\text{Al}^{3+}$  for  $\text{Mg}^{2+}$  in the octahedral sheet generates an excess of negative charges that are normally counterbalanced by cations ( $\text{Na}^+$  or  $\text{K}^+$ ) residing in the interlayers (Fig.1) [11].

The organically modified clays are prepared by the addition of long chain aliphatic quarternary ammonium or phosfonium cations to sheet mineral inorganic clays. An ion exchange process is utilized to displace the inorganic cations (e.g. sodium) with organic cations, thus improving the compatibility of the organosilicate with an organic environment [2].

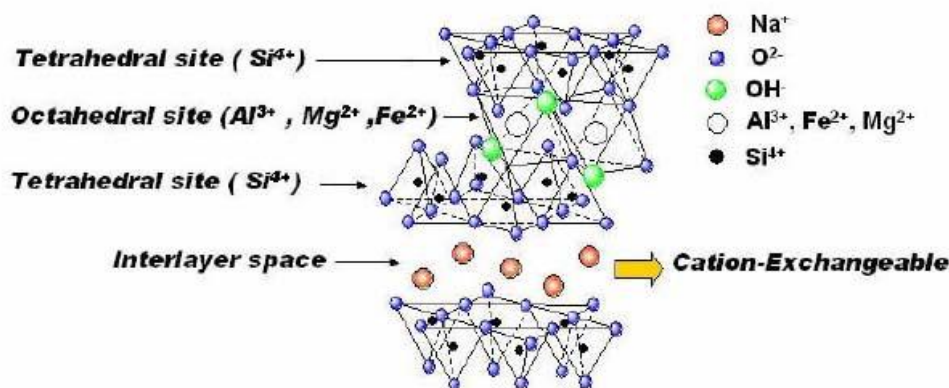


Fig. 1. Structure of layered clays

When mixed into the host polymer, exfoliation (breaking apart) of the nanophase organoclay can occur whereby the silicate sheets lose their attraction to each other. A very large increase in surface area occurs and, if the chemistry properly designed, the polymer chains can become attracted to the clay sheets. A hybrid inorganic-organic material is produced with altered properties that vary depending on the level of dispersion, the organic cation, the silicate, and the host polymer. Also can be used nonionic substances to modify clays that can be attracted to clay's surface mainly by hydrogen bonds. In some cases organoclays obtained by nonionic surfactants are more chemically stable than organoclays obtained using cation modifiers (Fig. 2) [12].

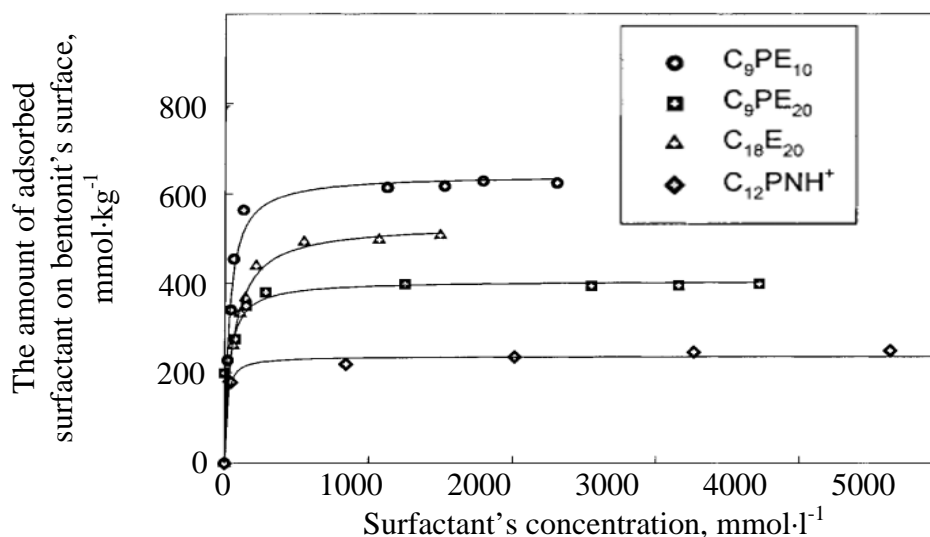


Fig. 2. I – the adsorptions of different modifiers on clay's surface

Desorbability of surfactants from bentonite depends on the mechanism of adsorption. A desorption hysteresis is generally observed when cationic surfactant is adsorbed via ion exchange (Fig. 2 II). The desorbability of surfactants from bentonite was compared by consecutively washing the organobentonite with deionized water. The nonionic surfactants in bentonite are relatively resistant to desorption; >80% were still adsorbed after seven consecutive washes. However, for cationic surfactants, washing resulted in 25% desorption. Apparently, the cumulative effect of hydrogen bonding between individual ethylene oxide units and the bentonite surface makes organobentonite derived from nonionic surfactant chemically more stable than organobentonite derived cationic surfactant.

Their makeup is such that they can be transformed into new materials possessing the advantages of both organic materials, such as light-weight, flexibility, and good moldability, and inorganic materials, such as high strength, heat stability, and chemical resistance. The incorporation of organic/inorganic hybrids can result in materials possessing excellent stiffness, strength and gas barrier properties with far less inorganic content than is used in conventionally filled polymer composites: the higher the degree of delamination in polymer/clay nanocomposites, the greater the enhancement of these properties [5].

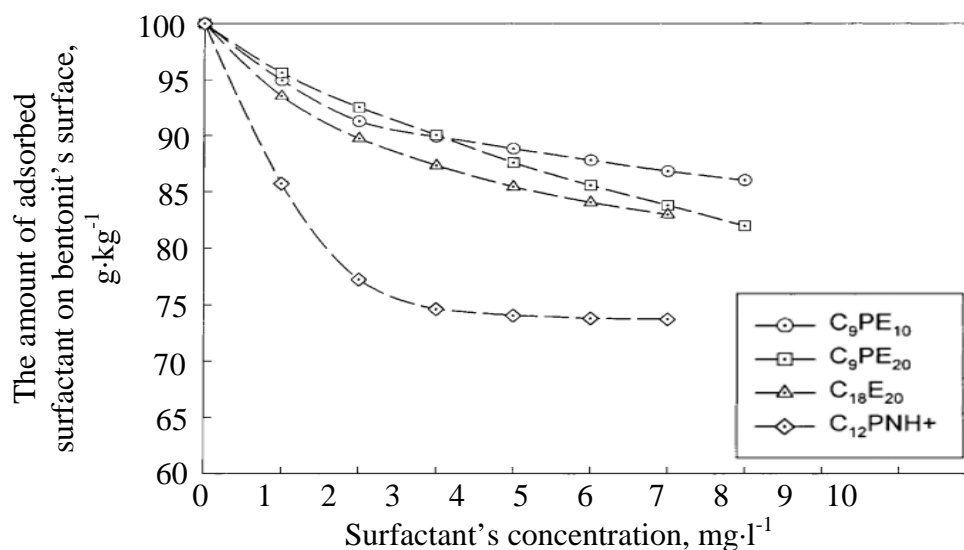


Fig. 2. II – the desorptions of different modifiers on clay's surface, where: C<sub>9</sub>PE<sub>10</sub> – C<sub>9</sub>H<sub>19</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub> CH<sub>2</sub>O)<sub>10</sub>OH; C<sub>9</sub>PE<sub>20</sub> – C<sub>9</sub>H<sub>19</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub> CH<sub>2</sub>O)<sub>20</sub>OH; C<sub>18</sub>E<sub>20</sub> – C<sub>18</sub>H<sub>37</sub>(CH<sub>2</sub> CH<sub>2</sub>O)<sub>20</sub>OH; C<sub>12</sub>PNH<sup>+</sup> – C<sub>12</sub>H<sub>25</sub>C<sub>6</sub>H<sub>4</sub>NH<sup>+</sup>Cl<sup>-</sup>

At present time have been synthesized a lot of different polymer nanocomposite materials based on various kinds of polymer materials and natural inorganic fillers. The amount of such works increases very intensively (Table 1).

**Table 1. Nanocomposites based on organoclay**

Name of polymer	Shorthand notation	Literature
Polyacrilate	PAC <sub>r</sub>	[13]
Polyamide	PA	[3, 14, 15]
Polybenzoksazole	PBO	[16]
Polybutyleneterephthalate	PBT	[2, 4, 18]
Polyimide	PI	[19]
Polycarbonate	PC	[20]
Polymethylmetacrilate	PMMA	[21]
Polypropylene	PP	[22, 23]
Polystyrene	PS	[21]
Polysulfone	PS <sub>n</sub>	[24]
Polyurethane	PU	[25]
Polyethyleneterephthalate	PET	[26]
Polyethylene	PE	[27]
Epoxy	EP	[28]

Several methods have been used to obtain polymer nanocomposites by using organoclays [29-32], i.e. solution intercalation [33-39], melt intercalation [40, 41], and in situ interlayer intercalation [30, 42, 43]. Among them, in situ interlayer polymerization relies on swelling of

the organoclay by the monomer, followed by in situ polymerization initiated thermally or by the addition of a suitable compound. The chain growth in the clay galleries accelerates clay exfoliation and nanocomposite formation.

This technique of in situ interlayer polymerization is also particularly attractive due to its versatility and compatibility with reactive monomers and is beginning to be used for commercial applications. However, there is ample evidence that nanocomposites can also be formed by melt processing in extruders. There are many reasons why melt processing may be more preferred method for producing nanocomposites for commercial use. Additionally, other approaches, such as the sol-gel process [44, 47] and monomer/polymer grafting to clay layers, have resulted in organic/inorganic polymer hybrids.

In the process of melt intercalation, the layered silicate is mixed with a molten polymer matrix. If the silicate surfaces are sufficiently compatible with the chosen polymer, then the polymer can enter the interlayer space and form an intercalated or an exfoliated nanocomposite. Otherwise, in situ intercalation polymerization is a method based on the use of one or more monomers that may be in situ linearly polymerized or cross linked and was the first method used to synthesize polymer-layered silicate nanocomposites based on polyamide 6. The in situ intercalation method relies on the swelling of the organoclay due to by the monomer, followed by in situ polymerization initiated thermally or by the addition of a suitable compound. The chain growth in the clay galleries triggers clay exfoliation and nanocomposite formation. Thus, an advantage of the in situ method is the preparation of polymer hybrids without physical or chemical interactions between the organic polymer and the inorganic material.

According to the early work of Giannelis [49], in general two types of hybrid structures can be obtained upon PCN preparation: *intercalated*, in which a single, extended polymer chain is intercalated between the silicate layers, resulting in a well-ordered multilayer with alternating polymer/inorganic host layers and a repeat distance of a few nanometers, and *disordered* or *delaminated*, in which the silicate layers (1 nm thick) are exfoliated and dispersed in a continuous polymer matrix (Fig 3). The best performances are commonly observed for the exfoliated nanocomposites; the two situations can, however, coexist in the same material. In any case, to make a successful nanocomposite it is very important to be able to disperse the inorganic material throughout the polymer. If a uniform dispersion is not achieved, agglomerates of inorganic materials are found within the host polymer matrix, thus limiting improvement.

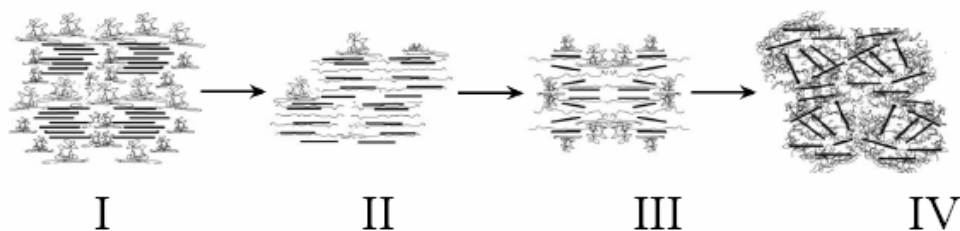


Fig. 3. Schematic illustration of nanocomposite formation

Unseparated MMT layers, after introduction into the polymer, are often referred to as tactoids. The term intercalated describes the case where a small amount of polymer moves

into the gallery spacing between clay platelets, but causes less than 2-3 nm separation between the platelets. Exfoliation or delamination occurs when polymer further separates the clay platelets e.g. by 8-10 nm or more. A well-delaminated and dispersed nanocomposite consists of delaminated platelets distributed homogeneously in the polymer [4, 5, 49, and 50].

One of the methods to study the dispersion of organoclay in nanocomposite is wide-angle XRD-diffraction. Thus, on figure 4 are shown XRD-data obtained for  $\text{Na}^+$ MMT, modified clay and PBT-fibers with different loading of organoclay.

The characteristic peak for pristine clay,  $\text{Na}^+$ MMT, appears at  $2\theta=8.56^\circ$  ( $d=1.2$  nm). For  $\text{Na}^+$ MMT reacted with alkyl amine, NCT-MMT, this peak is broadened and shifted to  $2\theta=3.98^\circ$  ( $d=2.6$  nm), suggesting that the clay is swollen to the range of the  $d$  spacing. In general, a greater interlayer spacing should be advantageous in the intercalation of polymer chains. It should also lead to easier dissociation of the clay, which should result in hybrids with better dispersions of clay. In addition to the main diffraction peak, an additional small peak is observed at  $2\theta=7.13^\circ$  ( $d=1.43$  nm). This secondary peak may be related to the XRD spectra of the organoclay itself. Fig.3 also shows the X-ray diffraction (XRD) curves of pure PBT and of PBT hybrid fibers with 2–5 wt% organoclay loadings. Pure PBT synthesized with an MMT interlayer exhibits its usual XRD peaks. However, in the cases of the 2 and the 3 wt% PBT hybrids, the curves show no characteristic organoclay peaks in the range of the  $2\theta=2-8^\circ$ ; that is, the peak corresponding to the basal spacing has disappeared. In the cases of the PBT hybrids with 4 and 5 wt% organoclay loadings, however, a small peak is observed at  $2\theta=5.44^\circ$  ( $d=1.88$  nm). This indicates that agglomeration of a small part of the clay has occurred in the PBT matrix [4].

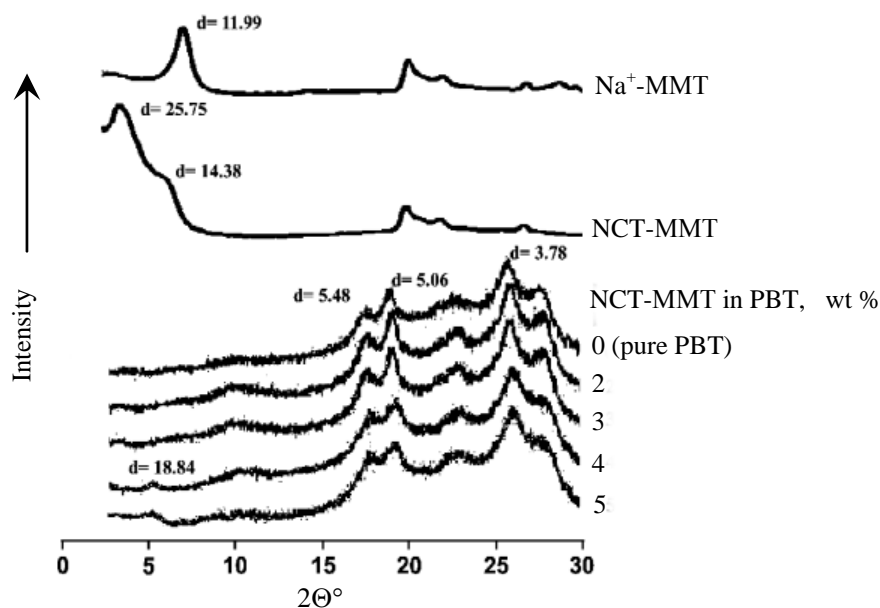


Fig. 4. XRD patterns for clay, organoclay, and PBT hybrid fibers with various organoclay contents

XRD-data also were obtained for other polymers (Fig. 5) [4, 49, and 50]. XRD is most useful for the measurement of the  $d$ -spacing of ordered immiscible and ordered intercalated

polymer nanocomposites with clay, but it may be insufficient for the measurement of disordered and exfoliated materials that give no peak. The organoclay dispersion in also has to be crosschecked further by using the SEM and TEM data [53, 54].

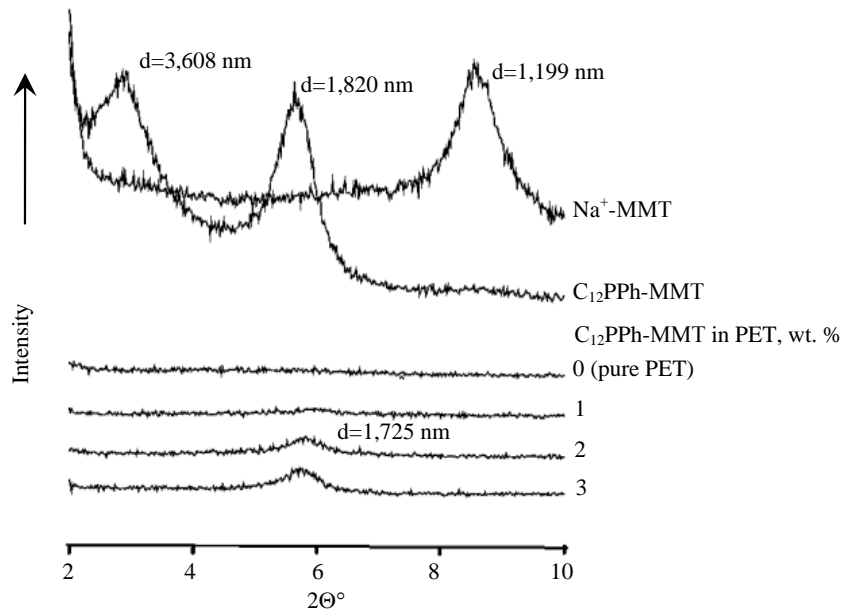


Fig. 5. XRD-data for clay, organoclay and nanocomposite PET/organoclay

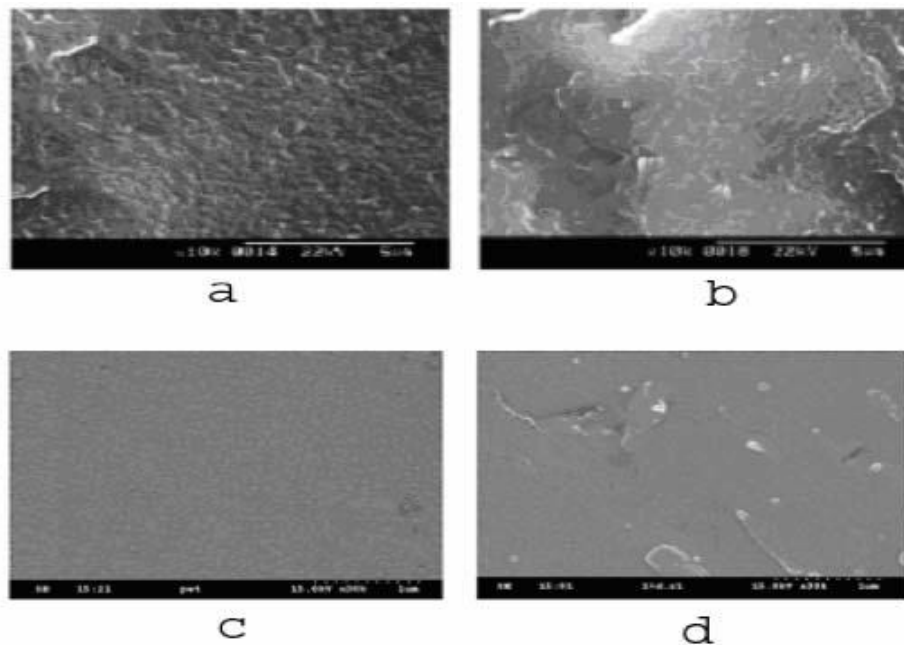


Fig. 6. SEM photomicrographs of (a) 0% (pure PBT); (b) 3% organic-MMT in PBT hybrid fibers; (c) 0% (pure PET); (d) 3% organic-MMT in PET hybrid fibers

SEM micrographs of the fractured surfaces of PBT hybrid fibers prepared with different clay contents are compared in Fig. 6, 7. The micrographs of the pure PBT/PET (Fig. 6(a, c)) and the PBT/PET hybrid fiber containing 3 wt% organoclay (Fig. 6(b, d)) show smooth surfaces due to better dispersed clay particles.

Conversely, fig. 7(a, b, c, d) show voids and some deformed regions that may result from the coarseness of the fractured surface. However, the fractured surfaces were more deformed when higher contents of organoclay were used in the hybrids. This is probably a consequence of the agglomeration of clay particles [55, 56].

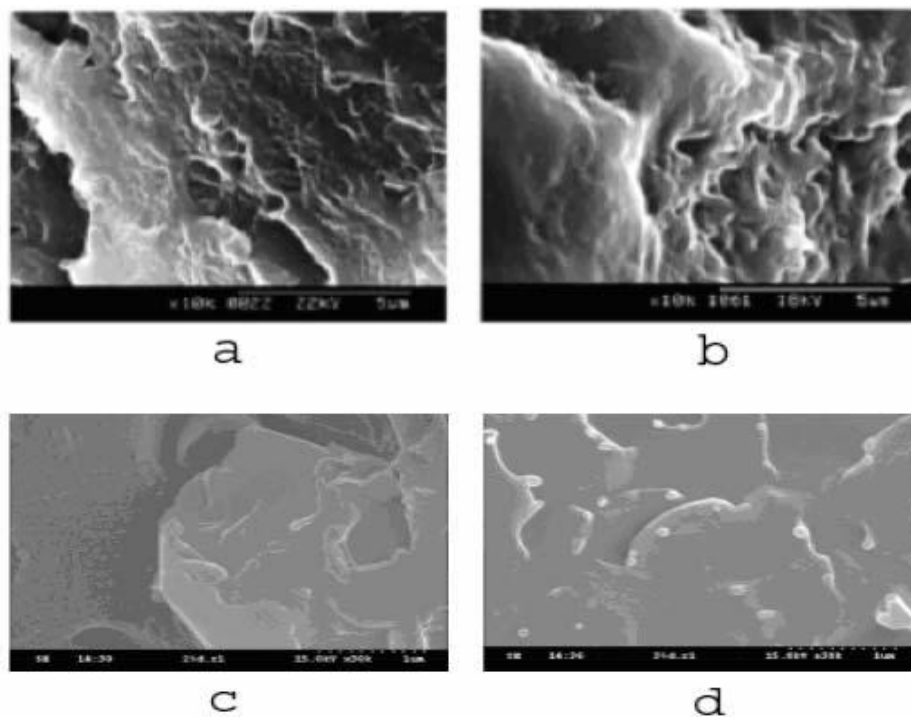


Fig. 7. SEM photomicrographs of (a) 4% (pure PBT); (b) 5% organic-MMT in PBT hybrid fibers; (c) 4% (pure PET); (d) 5% organic-MMT in PET hybrid fibers

More direct evidence for the formation of a true nano-scaled composite was provided by TEM analysis of an ultramicrotomed section. The TEM micrographs are presented in Fig. 8, 9. The dark lines are the intersections of 1 nm-thick clay sheets, and the spaces between the dark lines are the interlayer spaces. Some of the clay layers of Fig. 6 show individual dispersion of delaminated sheets in the matrix, as well as regions where the regular stacking arrangement is maintained with a layer of polymer between the sheets. Although a face-to-face layer morphology is retained, the layers are irregularly separated by, 4–10 nm of polymer.

For the 4 and the 5 wt% organoclay-loaded PBT/PET hybrid fibers (Fig. 9) however, some of the clay is well dispersed in the PBT/PET matrix, and some of it is agglomerated to a size of approximately 4-8 nm. This is consistent with the XRD results shown in Fig. 4, 5.



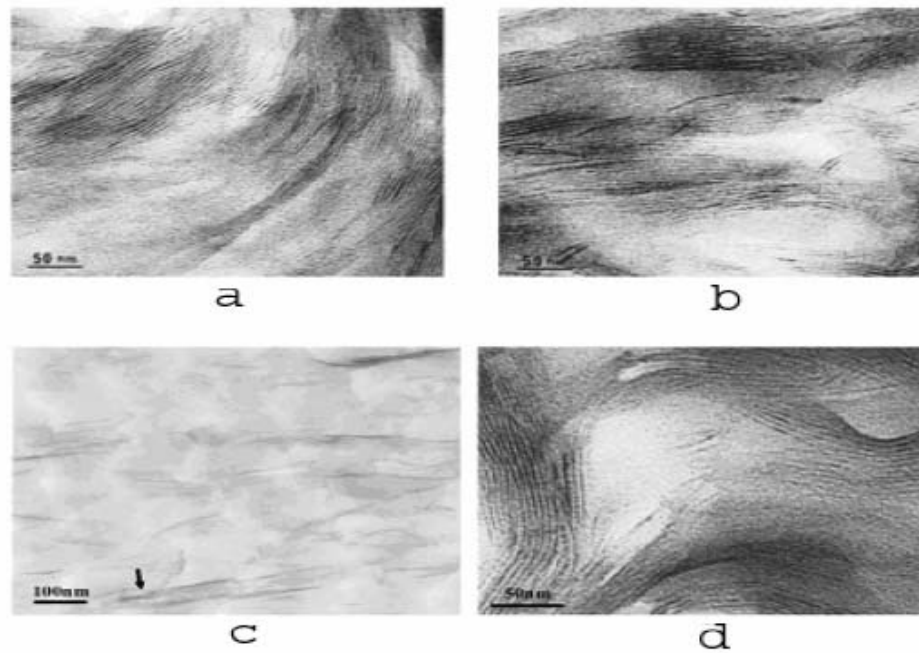


Fig. 8. TEM photomicrographs of (a) 2% organoclay in PBT; (b) 3% organoclay in PBT; (c) 1% organoclay in PET; (d) 1% organoclay in PET

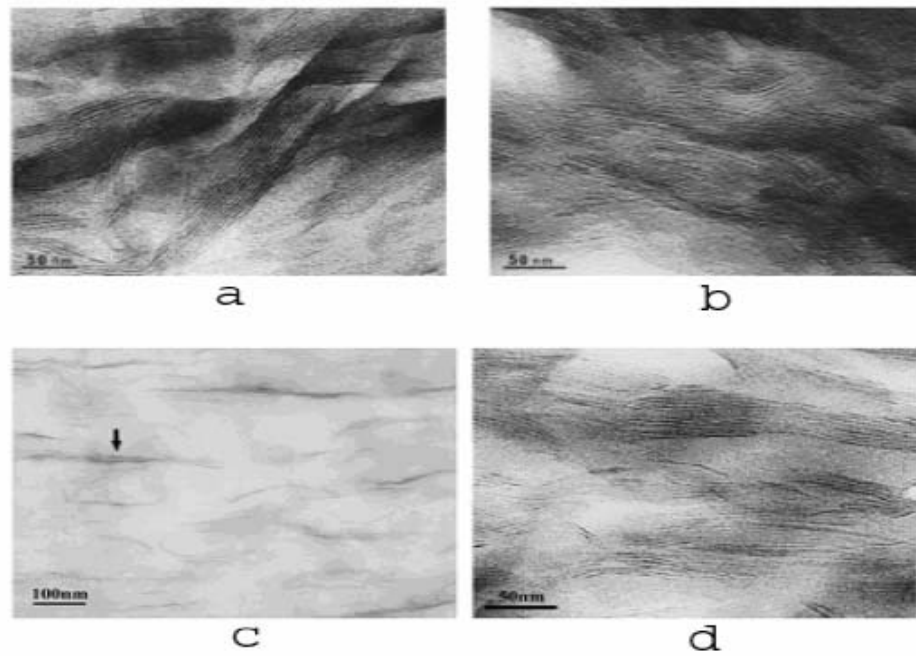


Fig. 9. TEM photomicrographs of (a) 4% organoclay in PBT; (b) 5% organoclay in PBT; (c) 3% organoclay in PET; (d) 3% organoclay in PET

From the results of XRD and electron micrographs, the morphology at a low organoclay content (<3 wt %) presents a mixture of intercalated and partially exfoliated features. The dispersion is better at a lower organoclay loading than at a high organoclay loading.

Using of organoclays as nanoparticles in polymer materials can change such properties as glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ) and decomposition temperature ( $T_d$ ), ultimate tensile strength (Ult. Str.), initial modulus (Ini. Mod.), percent of elongation at the break (E.B.), gas-, moisture barrier properties.

The thermal and mechanical properties of PBT and PET (polyethylene terephthalate) hybrids with different contents of organoclay are listed in Table 2.

The glass transition temperatures ( $T_g$ ) of the PBT hybrids increased from 27 to 33 °C with increasing clay loading from 0 to 2 wt% and then remained fairly constant up to 5 wt% organoclay. The increase in the  $T_g$  of these hybrids may be the result of two factors [57-60]. First, the effect of a small amount of dispersion of the clays on the free volume of PBT is significant and has an influence on the glass transition temperature of the PBT hybrids. Second, confinement of intercalated polymer chains within the clay galleries prevents segmental motions of the polymer chains. The endothermic peak of pure PBT appears at 222 °C and corresponds to the melting temperature ( $T_m$ ). Similar to the result for  $T_g$ ; the DSC thermograms show that the value of  $T_m$  increases from 222 to 230 °C with increasing organoclay content up to 2 wt%, and then remained constant for additional organoclay loading up to 5 wt% (Table 2). This increase in the thermal behavior of the hybrids may result from the heat insulation effect of the clay layer structure, as well as from the interaction between the organoclay and PBT molecular chains [59, 60].

**Table 2. Main properties of polymer nanocomposites**

Properties	Composite structure									
	Polybutylene terephthalate +					Polyethylene terephthalate +				
	NCT-montmorillonite					C <sub>12</sub> PPh-montmorillonite				
	Organoclay quantity, %									
	0	2	3	4	5	0	1	2	3	
Viscosity, Dl/g	0,84	1,16	0,77	0,88	0,86	1,02	1,26	0,98	1,23	
$T_g$ , °C	27	33	34	33	33	---	---	---	---	
$T_m$ , °C	222	230	230	229	231	245	247	245	246	
$T_d$ , °C	371	390	388	390	389	370	375	384	386	
$W_{IR}^{600c}$ , %	1	6	7	7	9	1	8	15	21	
Ultimate strength, MPa	41	50	60	53	49	46	58	68	71	
Initial modulus, GPa	1,37	1,66	1,76	1,80	1,86	2,21	2,88	3,31	4,10	
Percent of elongation at break, %	5	7	6	7	7	3	3	3	3	

Thermal stability of nanocomposites based on PBT/PET studied by thermo gravimetric analysis (TGA) is shown in table 2 and figures 10, 11 [4, 5].

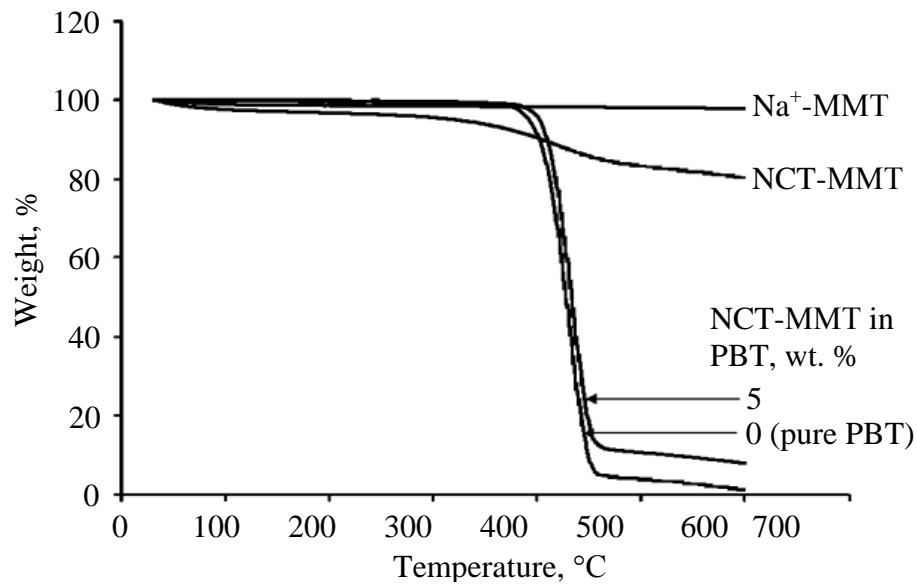


Fig. 10. TGA curves of montmorillonites, PBT and nanocomposite PBT/organoclay

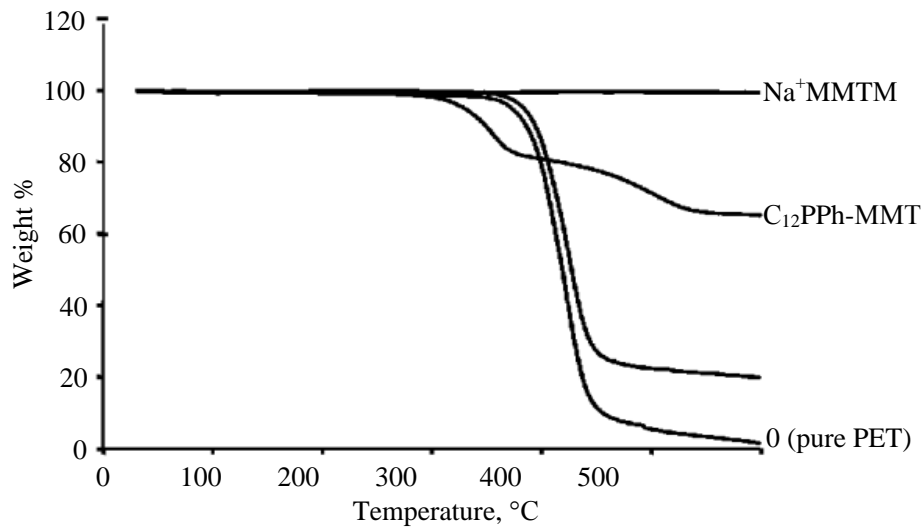


Fig. 11. TGA curves of montmorillonites, PET and nanocomposite PET/organoclay

The weight loss due to the decomposition of PBT and its hybrids was nearly the same until a temperature of 350°C (Fig. 10). Above 350°C,  $T_D$  was influenced by the organoclay loading in the hybrids. The addition of clay enhanced the performance by acting as a superior insulator and as a mass-transport barrier to the volatile products generated during decomposition [63, 64, and 65]. This kind of improvement in thermal stability has also been observed in many systems of hybrids [66, 67]. The weight of the residue at 600°C increased with increasing clay loading from 0 to 5%, ranging from 1 to 9%. This enhancement of the char formation is ascribed to the high heat resistance due to the clay itself. Considering the above results, we find it consistently believable that the introduction of an inorganic clay

component into an organic polymer can improve polymer's thermal properties due to the good thermal stability of the clay.

As it shown in table 2 at DR (draw rate) = 1, the ultimate tensile strength of the PBT/NCTMMT hybrid fibers increases with the addition of clay up to a critical clay loading, and then decreases above that critical content. For example, the strength of 3 wt% PBT hybrid fibers is 60 MPa, which is about 50% higher than that of pure PBT (41 MPa). When the amount of organoclay in PBT reaches to 5 wt%, the strength has decreased again to 49 MPa. This suggests that the NCT-MMT domains are more agglomerated above 3 wt% organoclay content in the PBT matrix [61, 68, and 69].

However, the initial modulus monotonically increased with increasing organoclay content in the PBT (Table 2). The value of the initial modulus increased constantly from 1.37 to 1.86 GPa with increasing NCTMMT content up to 5 wt%. This enhancement modulus is ascribed to the high resistance exerted clay itself. Additionally, the stretching resistance and oriented backbone of the polymer chain contributes to the enhancement of the modulus. Percent elongations at the break of all hybrids were 7%. These values remained constant for organoclay loadings from 2 to 5 wt%.

As Table 2 shows, the values of the strength and the initial modulus for pure PBT fibers were enhanced with increasing DR. However, as expected for the case of a flexible coil polymer, the increases in the tensile strength and the modulus with increasing DR were insignificant for pure PBT. Table 3 shows that for pure PBT, the strength and the modulus values increased. On the other hand, the values of the strength and the initial modulus of the hybrid fibers decreased with increasing DR. For the hybrid with 3 wt% organoclay, for example, when the DR was increased from 1 to 6, the ultimate strength and the initial modulus decreased. These trends with increasing DR were observed in all systems containing 2–5 wt% organoclay. This declination in the tensile properties seems to be the result of debonding between the organoclay and the PBT and the presence of many micro-sized voids due to excess stretching of the fibers [71-73].

**Table 3. Effect of the DR on the tensile properties of PBT nanocomposite fibers**

Organoclay loading, %	Ultimate strength, MPa			Initial modulus, GPa		
	DR=1	DR=3	DR=6	DR=1	DR=3	DR=6
0 (pure PBT)	41	50	52	1,37	1,49	1,52
3	60	35	29	1,76	1,46	1,39

Finally it has to be noted that the amount of studies devoted to the polymer nanocomposite materials increases very intensively. It was shown the ability of using of practically all kinds of polymer materials. Common understanding about investigation methods and structure of nanocomposite polymer materials, about relationships between properties and specific structure of nanocomposites is formed. Increasing of studies in this field proves that it will become very perspective approach to prepare in industrial scales new polymer materials with a lot of improved properties.

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*Chapter 2*

## **STRUCTURE AND PROPERTIES OF COMPOSITIONS ON THE BASIS OF MIXES OF EPOXYNOVOLAIC AND PHENOLFORMALDEHYDE PITCHES**

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### **ABSTRACT**

The results of studying laws of processes of structure – formation in the diluted and concentrated solutions of mixes of epoxy novolac (EV) and phenolformaldehyde (PF) pitches in various diluents environments and in films are presented in this work. The objectives are to choose an optimal pairs of compounds and to select the time - temperature conditions of producing a wearproof working layer of hard magnetic disks.

**Keywords:** epoxy novolac pitches, phenolformaldehyde pitches, characteristic viscosity

### **INTRODUCTION**

Materials on a basis of epoxy novolac pitches possess a unique complex of technological and operational properties. High adhesion to many metals, small shrinkage in process of solidification, chemical stability and high durability – all this provides their successful use as binding working layers of magnetic recording medium [1].

Studying laws of formation of mesh structure and properties of the unfilled and filled mixes of epoxy novolac and phenolformaldehyde pitches during their solidification allows to establish the mechanism of solidification process of reactionary mix and to offer optimal time

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– temperature modes of producing a working layer of hard magnetic disks with high operational characteristics.

The results of studying laws of processes of structure – formation in the diluted and concentrated solutions of mixes of epoxynovolaic (EV) and phenolformaldehyde (PF) pitches in various diluents environments and in films are presented in this work. The adjectives are to choose an optimal pairs of compounds and to select the time - temperature conditions of producing a wearproof working layer of hard magnetic disks.

## THEORY

On the basis of changing values of characteristic viscosity  $[\eta]$  (which are associated with the rotation and elastic – viscous deformation of macromolecular balls in a stream of solvent) and Haggings's constant one may determine the thermodynamic affinity of solvent to studied polymers or their mixes [2,3].  $[\eta]$  is a measure of additional losses of energy during spreading of the solution). Haggings's constant depends on a degree of interaction of polymeric molecules with solvent and is determined by the formula

$$k' = \frac{\eta_{cp} - [\eta]}{[\eta]^2 \cdot c} \quad (1)$$

Negative deviations from additive values of characteristic viscosity  $[\eta]$  witnessing bad overlapping of EV and PF molecules for solutions of these polymers in mixes of the solvents containing etiltseozolv, isoformon, cyclohexanon and dimethylformamide in various parities are found. Values of Haggings's constant  $k'$  appear to have positive deviation from the additivity for mentioned solutions testifying that energy of interaction of molecules of the dissolved polymers with molecules of diluent medium exceeds energy of interaction polymer 1 – polymer 2. This indicates that interaction between molecules of solvent and molecules of both epoxynovolaic and phenolformaldehyde pitch is more preferable than interactions between molecules of the pitches dissolved in such solutions, i.e. speaks about bad overlapping of polymers in these solvents.

The best overlapping of epoxynovolaic pitches with phenoformaldehyde was attained in diluent medium containing isoformon and etiltseozolv in the ratio 2:1. As is seen from fig. 1, change of value  $[\eta]$  in solutions of EV:PF mixes obeys the additive law for all structures:

$$[\eta] = [\eta]_1 \cdot W_1 + [\eta]_2 \cdot W_2, \quad (2)$$

where  $W_1$  and  $W_2$  – weight fractures of pitch compounds;  $[\eta]_1$  and  $[\eta]_2$  – characteristic viscosities of components.

The Haggings's constant  $k'$  changes with negative deviation from additivity for these solutions. That points good solubility of EV and PF in each other without formation of aggregated particles.

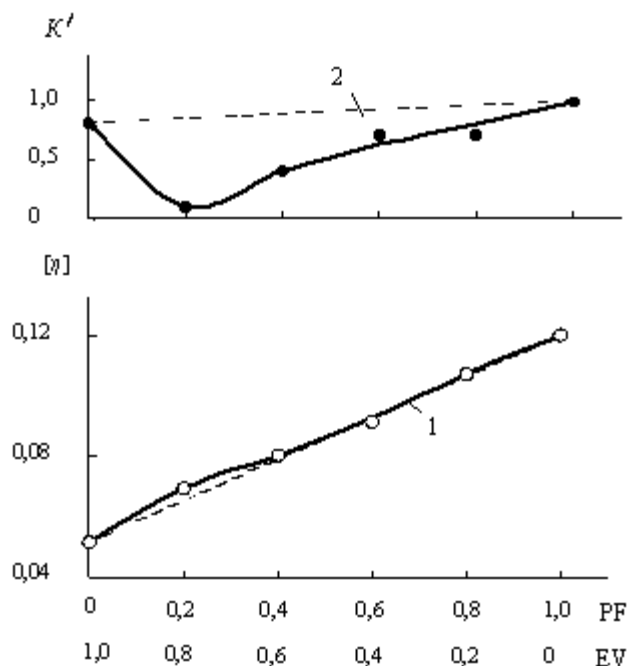


Figure 1. Dependencies of  $[\eta]$  (1) and  $K'$  (2) via composition of mix of EV and PF pitches in diluent medium containing isofofon and etiltseozolv in ratio 2:1

Basing mentioned we recommend diluent mix which contains isofofon and etiltseozolv in ratio 2:1 to obtain the solution of epoxynovolaic and phenolformaldehyde pitches at manufacturing magnetic varnish for producing hard magnetic disks (HMD). Also we recommend to mix EV and PF according to the ratio 4:1 to be used as binding working layer of HMD because such pair of pitches has least value  $k' = 0,14$ .

Interaction of molecules of the dissolved substance with each other results in sharp increase of viscosity in the concentrated solutions of polymers comparing with viscosity of the diluted solutions.

Interest to rheological properties of the concentrated solutions of studied mixes EV:PF is caused not only by technological problems of their processing in a product, but also by an opportunity to receive the information on their structure which can be presented as fluctuation grid formed by more or less densely packed units or molecular complexes. Solvent molecules are supposed to be distributed in that grid.

## EXPERIMENT

Samples were examined on rotational viscometer «REOTEST» with working unit cylinder – cylinder in an interval of temperatures 298÷338 K. Measurements of viscosity of the concentrated solutions of a mix of epoxynovolaic and phenolformaldehyde pitches have shown that dynamic viscosity  $[\eta]$  decreases with raise in temperature. It testifies that supramolecular structures are destructed under action of thermal motion in studied solutions. Increase of concentration of solutions, on the contrary, increases viscosity and the strain of

shift caused by growth of both number and sizes of aggregates. Apparently from fig. 2, the action of second factor prevails at lower temperatures (from 298 up to 313 K), though effect of first factor determines structure of a solution at higher ones (from 318 up to 338 K).

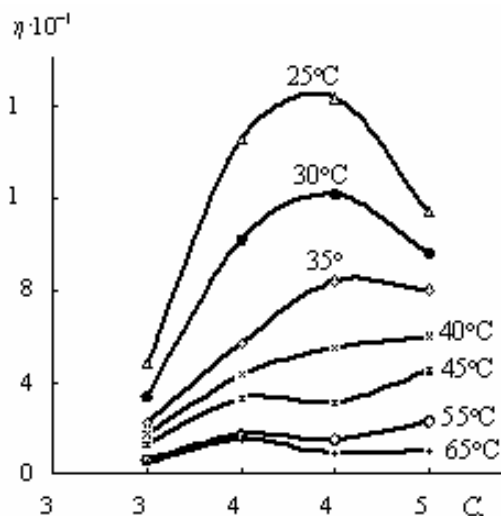


Figure 2. Concentration curve of dynamic viscosity  $\eta$  of solutions of mixed pitches EV:PF = 4:1 in medium isofofon : etiltseozolv = 2:1 at temperatures 25 ÷ 65 °C

Using Frenkel – Eiring formula expressing temperature dependence of viscosity

$$\eta = A \exp\{\Delta G_B / RT\} \quad (3)$$

we have calculated values of activation heat and activation entropy of viscous flux of studied solutions (see Table 1) using kinetic dependence  $\lg \eta \sim T^{-1}$ .  $\Delta G_B$  in (3) is the free activation energy of viscous flux.

It's seen from these data that there is the durability growth of supramolecular structure with raise in concentration up to 45 g / (100 ml). Such supramolecular structure is formed by molecular aggregates of dissolved polymers. Occurred aggregates also become ordered. The further increase in concentration leads to loosening of structures and to reduction of orderliness.

It follows from results, that for obtaining strong wearproof working layers of hard magnetic disks, in which the mix of epoxynovolaic and phenolformaldehyde pitches is used as binding, it is possible to recommend structures of magnetic varnishes with the content of a polymeric mix not more than 45 g / (100 ml).

**Table 1. Activation parameters ( $\Delta H_B$  and  $\Delta S_B$ ) of viscous flux of mix EV:PF = 4:1**

$C, \text{ g/100 ml}$	35	40	45	50
$\Delta H_B, \text{ kJ/mol}$	48,7	63,3	67,8	47,8
$\Delta S_B, \text{ kJ/mol}\cdot\text{K}$	54,8	93,6	108,3	43

The study of laws of formation of mesh structure aiming the choice of an optimal time – temperature mode of solidification of epoxynovolaic pitches, arranged within frameworks of Infra – Red spectroscopy, has shown that there is a formation of a spatial grid in the mechanism of interaction of epoxide groups (EG) of epoxinovolaic pitch with hydroxyl groups of phenolformaldehyde pitch (PFHG) [4].

The structural changes occurring in a polymer matrix during solidification are reflected in spectra of dielectric losses. There is a reduction of height of maxima of dielectric losses with the increase of solidification degree. The decrease of maxima corresponds to the process of vitrification of epoxide polymers and also to their displacement aside heats (fig. 3). Such change of spectra of a dielectric relaxation testifies that with increase in number of units of a chemical spatial grid the distance between crosslinkings decreases, that in turn leads to reduction of number of segments and increases height of a potential barrier of segmental motion, i.e. raises vitrification temperature of a polymer [5,6].

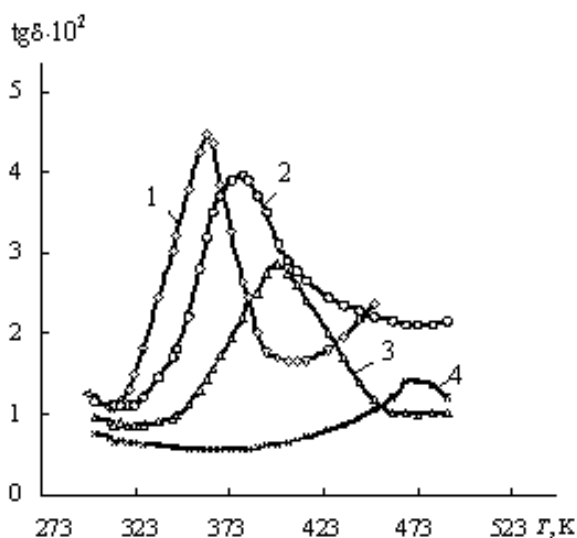


Figure 3. Temperature dependence of  $\text{tg}\delta$  of mix EV:PF = 4:1 of different solidification stages: 1 – stage I; 2 - stage II; 3 – stage III; 4 – stage IV

## DISCUSSION

Uniformity of distribution of units of a chemical spatial grid in volume of solidifying mix renders the big influence on thermostability of the investigated polymers.

It's seen from fig. 4 that process of thermooxidative destruction proceeds in three stages for all studied samples excepting one with maximal solidification depth. There were only two steps. Significant (up to 15 %) change of weight at 373-423 K for non – solidified sample on curve of thermogravymetry is associated with evaporation of solvents. Endothermic peak in same temperature interval on curve of differential thermoanalysis confirms this assumption for given sample. Either absence of losses of weight in these temperature areas of solidified samples serves as the certificate to that. The temperature of the beginning of weight losses of

studied samples raises from 563 K up to 588 K with growth of a solidification degree, then is reduced, reaching 533 K for a sample with the maximal depth of solidification. In process of growth of a solidification degree I and II stages of decomposition, caused by thermooxidative destruction of aliphatic part of polymer, approach on a temperature scale and merge after the end of solidification process, thus a share of weight losses of stage III grows.

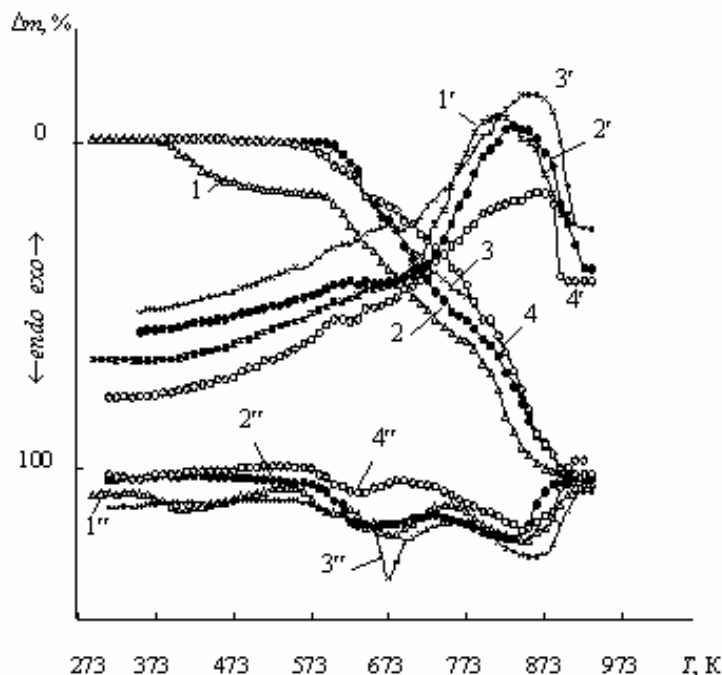


Figure 4. Curves of thermogravimetry analysis (1-4), differential thermoanalysis (1'-4') and differential thermogravimetry (1''-4'') of mix EV:PF = 4:1 of different solidification stages (I-IV)

The data obtained with help of thermogravimetry testify that there is an increase of density of samples due to growth of linear chains of suprapolymeric structures at first stages of solidification according described mode. Reduction of speed of weight losses of samples also proves that. Thus rise in temperature of the beginning of weight losses of samples is observed. The formation of a spatial grid at a subsequent stages of solidification results in the appearance of heat – setting processes and stressed portions of polymeric chains between chemical units. The increase in an overstrain of such places is apparently the reason of temperature decrease of the beginning of weigh losses of solidified samples. In this connection, it is rational to delay initial stages of solidification while the further process can be proceeded in more severe constraints.

Adsorption – adhesive interactions of polymer with a surface of a filler limiting mobility of its kinetic fragments in a boundary layer results in increase of activation energy of relaxation process in this area and broadening of the spectrum of times of a structural relaxation [7].

Presence of such structural heterogeneity in the polymeric matrix caused by presence of filler, renders considerable influence on processes of structurization during solidification of mixes of epoxynovolaic and phenolformaldehyde pitches [8, 9].

The study of solidification process of epoxynovolaic pitches has shown (at the presence of magnetic particles  $\gamma\text{-Fe}_2\text{O}_3$ ) that filler accelerates the processes of structurization in a researched reactionary mix. And this influence on different stages of solidification is not identical. The influence of filler particles is insignificant on stage II of solidification when processes of growth of molecular chains play the prevailing role. Vice versa presence of filler particles accelerates this process on stage III of solidification when there is intensive formation of a spatial chemical grid. The influence of filler is negligible again on deep degrees of solidification, when the sizes of its particles exceed distance between crosslinkings (IV stage).

Due to upper – said it is reasonable to realize step – like mode of solidification of working layers of the hard magnetic disks containing mix of epoxynovolaic and phenolformaldehyde pitches as polymeric binding. Such a regime avails us to delay process not only on II, but also on III stage of solidification.

## CONCLUSION

On the basis of stated we've offered the solidification mode of a binding working layer of hard magnetic disks on the basis of a mix of epoxynovolaic and phenolformaldehyde pitches:

(293 K×1,5 hour)	(I)
+ (413 K×3 hour)	(II)
+ (453 K×2 hour)	(III)
+ (473 K×1,5 hour)	(IV)

It allows to achieve deep solidification degrees and is essential for reducing time of holding a composition at heats (473 K). The performed tests of hard magnetic disks, working layers of which contain a mix of epoxynovolaic and phenolformaldehyde pitches as a binding matrix, solidified on the specified mode have shown that they do not concede to foreign analogues on their physicomechanical and operational characteristics.

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*Chapter 3*

## CHAIN FRACTAL GEOMETRY AND DEFORMABILITY OF POLYMER COMPOSITES

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### ABSTRACT

It is shown, that the fractal geometry of chain part between its fixation points to a great extent is determined by the carbon plastics deformability. This is true also in relation to the density of cluster network of physical entanglements, which is also influenced on the value of fractal dimension of the mentioned chain part. The carbon plastics plasticity is controlled by state of polymeric matrix structure characterized by its fractal dimension.

**Keywords:** Carbon plastic; polyethylene; short fibres; deformability; plasticity, fractal dimension.

### INTRODUCTION

The ability to bear large strains with following full return at stress removal is property displayed at appropriate conditions by actually all substances consisted of long chain macromolecules [1]. What's more, this property is displayed by exclusively materials of such structure. It is important beyond narrow limits of the term "rubber elasticity", by which it is usually designated. The mentioned property acts at swelling of polymeric networks and polymer's deformation, in general not included in the rubber category, for example, semi-

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crystalline polymers, at viscoelastic behaviour of linear polymers in case of flow in liquid or amorphous state. The basis premise of molecular theory of rubber high-elasticity serves assumption, that the stress in rubbers is the result of deformation of covalent network chains, while the contribution of interaction between chains is negligible. Strictly speaking, this is not quite correct even for true rubbers [1] and what's more for polymers in glassy state. The theory of high-elasticity gives the following expression for estimation of limiting draw ratio  $\lambda$  of elastomers [2]:

$$\lambda = n_{st}^{1/2} \quad (1)$$

where  $n_{st}$  is statistical segments number on chain part between its fixation points (chemical cross-linking nodes, physical entanglements and so on).

For application of the considered conception to glassy polymers usually a number of empirical assumptions made accounting into consideration much stronger intermolecular in such systems. Edwards and Vilgis [3] offered sliding links conception, which assumes division of chain between entanglements on smaller fragments, which are fixed, but have significant internal freedom. This results to decrease of polymer's limiting strain in comparison with estimated one according to the equation (1). The authors [4] took into consideration physically strictly this factor by introduction in the equation (1) the exponent  $(D-1)$  instead of constant parameter  $1/2$ :

$$\lambda = n_{st}^{D-1} \quad (2)$$

where  $D$  is fractal dimension of chain part between its fixation points.

This dimension is varied in limits  $1 < D \leq 2$  and characterizes internal freedom degree (mobility) of pointed chain part. The purpose of present paper is the application of a model [4] for description of deformability of carbon plastics based on the high density of polyethylene (HDPE).

## EXPERIMENTAL

As a polymeric bonding agent HDPE of industrial production (GOST 16-338-85) with crystallinity degree 0.72, estimated by density measurements, and as filler – carbon fibres (CF) of mark Ural-24 were used. The volume content of CF  $\varphi_f$  in carbon plastics is varied in limits 0.038-0.303. A components blending is made on extruder ZSK-30 at the following technological regime: the temperature of the first zone is 408, the second – 413, the third – 428 and the fourth – 423 K. The specimens for studies in the form of dog-bone with base length 20 mm were manufactured by the method of compression molding on machine KUASY-100/25. In production process in machine cylinder the following temperature regime was maintained: the first zone – 423, the second – 428 and the third – 443 K. The temperature of casting of specimens was made on testing machine FRZ-100/1 of firm Heckert at the testing temperatures 293, 313, 333 and 353 K and strain rate  $10^{-2} \text{ s}^{-1}$ .

## RESULTS AND DISCUSSION

As the results of mechanical tension testing showed, limiting draw ratio of studied carbon plastics is decreased at the increase of carbon fibres volume content in interval  $\sim 6.0-1.1$ . In order to obtain quantitative interrelation of  $\lambda$  and  $D$  according to the equation (2), was made calculation  $D$  by the following method. The value of fractal (Hausdorff) dimension  $d_f$  of carbon plastics structure is determined according to the equation [5]:

$$d_f = (d-1)(1+\nu) \quad (3)$$

where  $d$  is dimension of Euclidean space, in which a fractal (obviously, in our case  $d=3$ ) is considered,  $\nu$  is Poisson's ratio, the value of which can be estimated on mechanical testing results with the aid of relationship [6]:

$$\frac{\sigma_Y}{E} = \frac{1-2\nu}{6(1+\nu)} \quad (4)$$

where  $\sigma_Y$  is yielding stress,  $E$  is elasticity modulus.

Then the value of characteristic ratio  $C_\infty$  has been determined, which is an indicator of polymer chain statistical flexibility according to the equation [7]:

$$C_\infty = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3} \quad (5)$$

Then the relative fraction of local order regions (clusters)  $\varphi_{cl}$  have been estimated with the aid of the equation [7]:

$$d_f = 3 - 6 \left( \frac{\varphi_{cl}}{SC_\infty} \right)^{1/2} \quad (6)$$

where  $S$  is cross-section area of macromolecule, which is equal to  $18.9 \text{ \AA}^2$  for polyethylenes.

And at last, the value  $D$  can be determined according to the following equation [7]:

$$\frac{2}{\varphi_{cl}^{red}} = C_\infty^D \quad (7)$$

where  $\varphi_{cl}^{red}$  is a reduced value  $\varphi_{cl}$ , taking in to account availability of filler and estimating according to the equation [8]:

$$\Phi_{cl}^{red} = \frac{\Phi_{cl}}{1 - \Phi_f} \quad (8)$$

The value  $n_{st}$  can be directly calculated from the equation [8]:

$$D = \frac{\ln n_{st}}{\ln(4 - d_f) - \ln(3 - d_f)} \quad (9)$$

It is obvious, that the parameter  $n_{st}$  characterizes density of cluster network of physical entanglements [7]. In Fig. 1 the dependence  $\lambda(n_{st})$  is shown, from which the increase  $\lambda$  at  $n_{st}$  raising follows, just as was expected from the equations (1) and (2). It is interesting, that this dependence breaks up into two parts with sharply differing slopes, for all that this transition is realized at  $n_{st} \approx 9$ . As it is known, mentioned value  $n_{st}$  is boundary between densely and loosely cross-linked polymers. The data of Fig. 1 suppose, that this classification is true and for cluster network of physical entanglements the value  $\lambda$  changes insignificantly and fracture is quasi-brittle and decrease of network density results to very fast rise  $\lambda$  in narrow interval  $n_{st}$ . It is necessary to note, that the form of shown in Fig. 1 dependence  $\lambda(n_{st})$  excludes the possibility of application of the equation (1) with constant exponent  $\frac{1}{2}$  for its correct description.

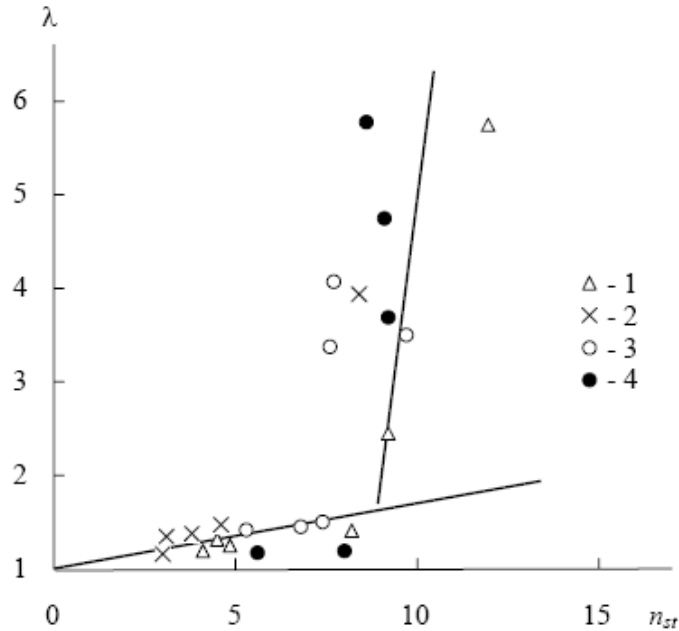


Figure 1. The dependence of limiting draw ratio  $\lambda$  on statistical segments number  $n_{st}$  on chain part between clusters for carbon plastics at testing temperatures: 293 (1), 313 (2), 333 (3) and 353 K (4)

In Fig. 2 the comparison experimental  $\lambda^e$  and calculated according to the equation (2)  $\lambda^T$  values of limiting draw ratio for studied carbon plastics at four testing temperatures are given. As can be seen, between  $\lambda^e$  and  $\lambda^T$  enough close correspondence is received and observed scatter of data relationship 1:1 is symmetrical and due to well known statistical character of fracture process.

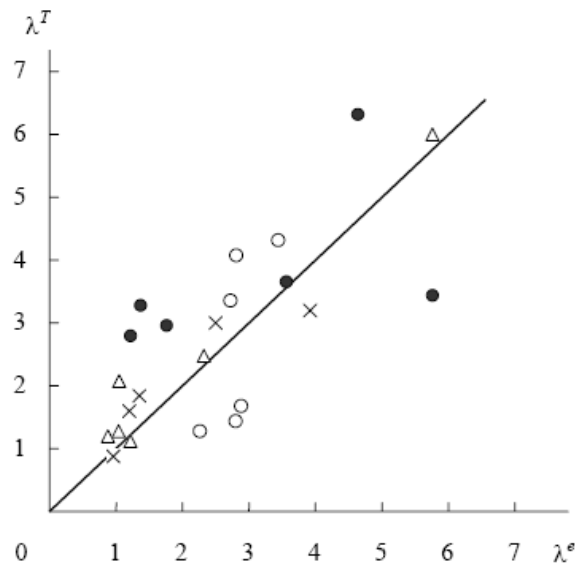


Figure 2. The comparison of experimental  $\lambda^e$  and calculated according to the equation (2)  $\lambda^T$  values of limiting draw ratio for carbon plastics. The straight line give relation 1:1. The notation is than one, that in Fig. 1

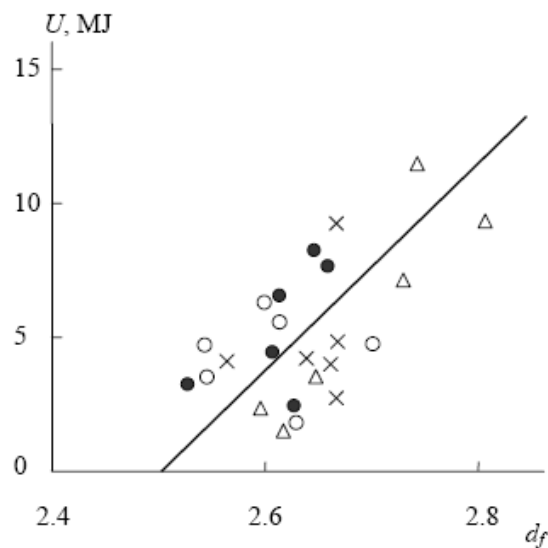


Figure 3. The dependence of fracture work  $U$  on structure fractal dimension  $d_f$  for carbon plastics. The notation is than one, that in Fig. 1

As it is known, the work of fracture  $U$ , characterizing expenditure of energy on material deformation up to failure, is one of the most important plasticity characteristics. In paper [5] it was shown, that the fracture character of solids is determined by the fractal dimension  $d_f$  of their structure: at  $d_f=2.50$  brittle fracture is realized, at  $d_f=2.50-2.67$  – quasibrittle (quasiductile) fracture and at  $d_f>2.70$  – ductile fracture. This classification allows to suppose plasticity increase characterized by value  $U$  at raising  $d_f$ . Actually, the dependence  $U(d_f)$  shown in Fig. 3 confirms this assumption. This dependence is linear, the increase  $U$  is observed at raising  $d_f$  and zero value  $U$  is reached at  $d_f=2.50$ , i.e., at brittle fracture. Since limiting (maximal) value  $d_f$  for real solid is equal to 2.95<sup>[5]</sup>, then this allows to estimate maximal value  $U$  for studied carbon plastics, which is equal to  $\sim 17$  MJ. The scatter of Fig. 3 data is again due to statistical character of fracture process.

## CONCLUSION

Consequently, the results received in present paper showed, that the fractal geometry of chain part between its fixation points to a great extent is determined by the carbon plastics deformability. This is also true in relation to the density of cluster network of physical entanglements, which is also influenced on the value of fractal dimension of the mentioned chain part. The carbon plastics plasticity is controlled by state of polymeric matrix structure characterized by its fractal dimension.

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