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BEHAVIOUR OF SOME IRRADIATED SOLID OXIDES IN DIFFERENT MEDIA AND IN THE PRESENCE OF ADDITIONS

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Abstract. It is known that the properties of filled polymeric glue composites to a great extent depend on the nature and surface properties (SP) of fillers. Usually solid oxides are used as fillers. For the first time the possibility of fillers SP modification exposed to the action of penetrating radiation of small doses (D) (H≈10^2 Gy) has been shown. The influence of preliminary irradiation (X-rays, gamma) of some mineral powders (SiO_2, MgO, TiO_2, ZnO, talc, kaolin) on their adsorption, suspension, rheologic properties and behaviour in the presence of some additions has been studied. It has been established that oxides SP dependence on irradiation D in absence,as well in the presence of different additions is described by the curves with extremums. They correspond to D_{ex} of the 10^2 Gy (10^4 rads) order.

Keywords: polymeric glue composites, filler, gamma-radiation, X-ray.

1. Introduction

It is well known that polymeric materials (PM) are used almost in all fields of human activity. The rapid growth of the modern technologies raises new requests with respect to PM. They concern their mechanical strength, adhesive and dielectric indexes, chemical stability *etc*. For this reason the production of new PM or their modification are actual problems.

In most cases polymeric composites contain fillers, mainly of inorganic nature. In this case the processes which occur on filler surface play a very important role. It is indispensable to establish their nature and mechanism in order to modify SP in such a way to realize only necessary processes under optimal conditions, indexes, chemical stability and so on. Modification means changes in the structure, *i.e.* reconstruction of crystalline lattices in the chemical nature of surface layers, *e.g.* formation of acid-base centers, change of their quantitave ratio.

At the present thermal treatment (in vacuum or in the air) and penetrating radiation ($D \approx 10^5$ Gy) are used to modify solids SP. But they have not wide application because the radiation-chemical yields (Y) of modification are low.

Taking into consideration this circumstance we have tried to increase the Y of solid oxides SP modification using irradiation of extremely small doses (D = 5–500 Gy) with the rate J = 0.5–1 Gy/s in the air at room temperatures.

2. Experimental

The objects of our studies were: SiO_2, ZnO, MgO, Al_2O_3, TiO_2, talc ($MgO{\cdot}H_2O{\cdot}4SiO_2$) and kaolin ($MgO{\cdot}2H_2O{\cdot}4SiO_2$) which differ by their "prohibited zone width" (from 3 to 10 eV), specific surfaces (S_{sp}), surface acid-base properties and ability to undergo phase transitions.

Different methods are used to determine quantitatively the structural and chemical changes which occur in oxides under the irradiation action. All experimental details are presented in [1-6].

Industrial liquid oligomers of epoxy resins (EP) and polyamide hardener (L-20) have been used.

Resin molecular mass (M_n) after adsorption is determined by isopiestic method in the form of $M_{n\,ads}/M_{n\,ini}$, where $M_{n\,ini}$ refers to M_n of initial resin [5].

Samples for radiation were prepared using standard vacuum equipment. They were calcined at 420 K in O_2 and rehydrated by water vapour. A part of each sample was used as a control sample.

Al_2O_3 sample was obtained by $Al(OH)_3$ calcination with boehmite as a transient phase. S_{sp} = 60 m²/g and d =3.53 g/cm³. Two samples of SiO_2 with S_{sp} = 175 and 340 m²/g were used. Other oxides were industrial samples with 99 % purity.

Adsorbed doses (D) were determined by time exposure. Dosage rate was 0.5–1.0 Gy/s.

Calculation of adsorption centers Y was carried out using the relation:

$$Y = \frac{\Delta \cdot 6 \cdot 10^{23}}{D \cdot 6.25 \cdot 10^{16}} \cdot \frac{1}{100eV}$$

where Δ is the number of formed adsorption centers (mol/kg); Y for water and OH-groups was determined analogically according to the data of mass loss α (mol/kg) during heating.

To determine adsorption of triethylamine (TEA) and stearic acid (SA), their benzene solutions were used. The adsorbed quantities were determined by titrating and weighing of the residue. Five parallel measurements were made for each case with errors of ± 5 %. The preliminary irradiated samples were used without any additional treatment [3].

The thermodesorption and dehydration (α value) were studied using chromatographic method (heating rater 15°/min, He was a carrier, gas rate was 10ml/min) and derivatographic method. Mass spectral thermodesorption and dehydration analysis were made to register particles with atomic mass 18.

The specific surface S_{sp} was determined by N_2 thermal desorption using chromatography [5].

Suspension viscosimetry was investigated using concentric-cylinder viscosimeter [1].

The density was measured using vacuum densimeter (50 ml) in heptane (sample weight was 10g). Weighting and temperature accuracy were $5 \cdot 10^{-4}$ g and 0.1°, respectively. The results reproducibility was ± 0.1 %.

3. Results and Discussion

3.1. The Influence of Irradiation on Solid Oxides at Room Temperatures

3.1.1. Radiation modification of SiO_2 [7]

The adsorption (AD) of triethylamine (TEA) and stearic acid (SA), mass losses (α) as the result of dehydration in the temperature range ΔT = 420–820 K (α), OH-groups concentration change on oxides surface, density (d) changes as the result of phase transitions are studied.

It has been established that:

(i) The dependence of all cited parameters on D may be expressed by curves which pass through extremum $D_{ex} \approx 150$ Gy.

(ii) Phase transitions occur:

$$SiO_2\,(glass)(amorphous) \underset{D>150\ Gy}{\overset{D\leq 150\ Gy}{\rightleftharpoons}} (quartz)(cryst)$$

It is known that the $d_{crys} > d_{amor}$. [8].

(iii) Preliminary dehydration of SiO_2 results in insensibility of surface layers with respect to the irradiation action.

Some data are given in Table 1.

Table 1

Dependence of α, TEA Ad and Y on D; D = 150 Gy

SiO_2	mol/kg		10^{-4} . Y for	
	α	TEA Ad	α	TEA Ad
Initial	1.00	0.27	-	-
Irradiated	1.40	0.71	8.1	4.4

3.1.2. Radiation modification of TiO_2 [9]

Similar results are obtained. In this case $D_{ex} \cong$ $\cong$ 300Gy. TEA Ad has maximum, while SA Ad has a minimum value at $D \cong$ 300Gy. So the irradiation results in acidic centers increase in TiO_2 superficial layers.

X-ray analysis showed that phase transitions occur:

$$Rutile \underset{D>300\ Gy}{\overset{D\leq 300Gy}{\rightleftharpoons}} (brookite)$$

Such phase transitions occur by heating the sample at 1023 K [10].

From these data it follows that the phase transition under the influence of irradiation is a reversible process.

For this reason when oxides are treated making use of irradiation great doses ($D \geq 10^5$ Gy) or high temperatures phase transitions, SP changes cannot be established as well.

3.1.3. Radiation modification of ZnO [11]

ZnO contains structural water from 8 to 15 μmol/m² [12]. The removal of physically adsorbed water begins from 340 K [13]. Noticeable water loss begins from 470 K [14]. Phase transitions and corresponding cover change of OH-groups are essential processes which occur over ZnO surface [15].

As the result of prolonged contact of ZnO with water vapors, $Zn(OH)_2$ is formed and it which under irradiation action loses water. But simultaneously phase transition occurs which acts on SP, particularly on its Ad ability. This process is reversible too. In fact TEA and SA Ad studies show that at D 300Gy TEA Ad has maximum, while SA Ad has a minimum value.

At D_{max} the radiation-chemical yield (Y), based on TEA Ad alteration, is $4.0 \cdot 10^2$/100 eV.

3.1.4. Radiation modification of Al_2O_3 [16]

TEA and SA Ad study on irradiated sample showed an increase of surface acidic centers concentration. This result agrees with literature data concerning diethylamine and pyridine Ad on thermotreated $Al(OH)_3$ [17]. TEA Ad has a maximum value at $D \geq$ 150Gy. SA Ad has a minimum value at the same D value.

At this D boehmite, as transient and reversible phase, prevails. The irradiation has small effect, if the Al_2O_3 sample is preliminary dehydrated by thermotreating at 590 K.

The increase of Na_2O content in Al_2O_3 results in decreasing radiation modification degree.

3.1.5. Radiation modification of MgO [18]

MgO has some specific characteristics:

(i) its surface unity contains more constitutional water [19];

(ii) on its surface Lewis acidic centers are absent [20];

(iii) it does not reveal electron-acceptor ability [21].

Irradiated MgO samples show extremal SP dependence on $D \cong 150$Gy. In this case TEA Ad has a minimum value, while SA has the maximum one. Again reversible radiation induced phase transition occurs at room temperatures:

$$\text{brucite.} \underset{D>300\ Gy}{\overset{D<300Gy}{\rightleftharpoons}} \text{periclase}$$

Such phase transition may be realized making use of thermal treatment at 670 K [22]. The radiation – chemical yield is based on weight loss α alteration(dehydration at 470–720 K), $Y \cong 10^4/100$ eV.

From the exposed material it follows: subjecting solid oxides to irradiation in the air and at room temperatures with D of the order 10^2 Gy becomes possible to modify their SP appreciably. This is very important especially in those cases when the oxides will be used as solid catalysts, dielectric thin film layers, adsorbents, fillers for glue composites.

3.2. Some Peculiarities of Rheological Properties of Irradiated Oxides Dispersions Obtained in Liquid Medium

Oxides suspensions have wide applications in obtaining filled PM: varnishes, paints, glues, pasts and so on. The filling efficiency to greater extent depends on the degree of filler (F) dispersion in the given liquid and on its compatibility with the polymer component.

These questions may be easily solved purposefully modifying SP, *e.g.* irradiating them under the above mentioned conditions.

The modification must favour to change the suspension viscosity (η) to the desired side, to enhance the systems aggregate stability which means stability of colloid particles.

Usually one may enhance colloid particles stability covering them with ionic polymers. They cover the particles with layers carrying the same charge. So the coagulation of the colloid may be prevented. As it was shown the irradiation favours to fulfill the cited action.

To verify the plausibility of the expressed proposition the influence of preliminary radiation-induced modification of mineral powders in different mediums and applied D has been studied.

MgO, ZnO, SiO_2, TiO_2, Al_2O_3, talc and kaolin are used as mineral powders and organic polar (alcohols, esters, ketones, acids) and non polar (hydrocarbons) liquids are used as dispersion media. The applied D is changed in the range 50–1000 Gy.

Suspensions may be characterized by their sedimentation stability. Its quantitative measure is the halftime of destruction (concretion) ($t_{1/2}$ in seconds).

Some obtained data are given in Table 2.

From stated data it follows:

(i) obtained suspensions of irradiated oxides are more stable;

(ii) with the increase of the dispersion medium polarity, suspension stability increases;

(iii) $t_{1/2}$ dependence on D may be expressed by a bell-shape curve which maximum corresponds to $D_{max} \approx 10^2$ Gy.

It is also established that suspension η obtained on the basis of kaolin in alcohols diminishes according to the following range:

$$C_2H_5OH > n\text{-}C_3H_7OH > iso\text{-}C_3H_7OH > n\text{-}C_4H_9OH > C_{10}H_{21}OH$$

Water results in η decrease. Suspension stability increases and η decreases when irradiated kaolin samples

Table 2

Suspensions $t_{1/2}$ dependence on D (J = 0.5 Gy/s)

Dispersed phase	Dispersion medium	$t_{1/2}$ in seconds at various dozes D (Gy)				
		0	**50**	**80**	**150**	**250**
Kaolin	CCl_4	0	17	20	18	12
	CH_3COCH_3	10	30	50	30	20
	C_2H_5OH	150	420	420	420	38
	$CH_3COOC_2H_5$	90	90	180	180	150
MgO	CH_3COCH_3	26	52	40	46	37
	C_2H_5OH	420	780	630	600	560

are used. The stated effect may be explained assuming that as the result of irradiation superficial acidic centers concentration is increased. In favor of this conclusion we may state the increase of Tea Ad and the decrease of SA.

It is interesting to note that SP changes remain for a long time. Study of suspension η dependence on [F] is not examined enough. The study of that question may present the possibility of determining adsorption layers thickness making use of rotation viscosimetry method.

Our experiments showed that suspensions η dependence on the content of non-irradiated and irradiated TiO_2 in *n*-BuOH is very complex (see Fig. 1).

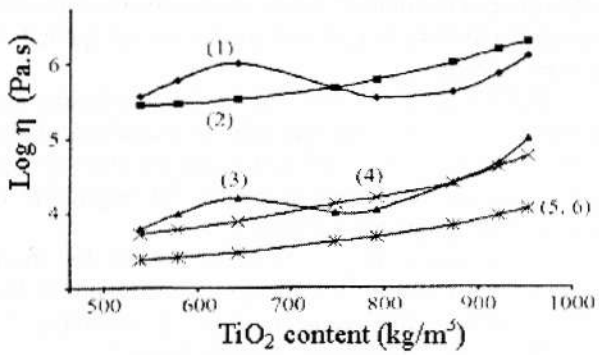

Fig. 1. Dependence of η on TiO_2 content in *n*-BuOH at different rates of shear (g, s^{-1}) using rotation viscosimetry method: g = 8.1 (1, 2), 1312 (3, 4), ∞ (5, 6). Curves (1, 3, 5) relate to irradiated TiO_2 samples (Dopt = 150 Gy, J =0.5 Gy/s, irradiation medium – air) and curves (2, 4, 6) – to the control samples

In this case $\gamma \to \infty$ corresponds to η_∞. It is determined by the formula $\eta = \eta_\infty + A\gamma^{-m}$ where A is an empiric constant, m is a parameter which depends on F dispersity degree.

The peculiarity of irradiated samples behaviour may be explained as follows. When F concentration is relatively low, usually η increases with [F] increase. Beginning from some "critical" concentration "file type" structures are formed in the system as the result of F-medium interactions which result in η enhance. Further [F] increase results in formed "file type" structures are destroyed and the noticed phenomena may not appear (curves 5, 6).

We assume that the exposed phenomena are bounded with the system aggregation stability. If this assumption is right then the volume of the precipitate (V_{pr}) which may be formed as the result of suspension destructions forces the action between *composers* particles. To verify the plausibility of this hypothesis V_{pr} or particle effective radius (r) dependence on the filling degree has been studied. Non-irradiated (control) and irradiated fillers (TiO_2) are used to obtain suspensions in *n*-BuOH. Sedimentation analysis is carried out to determine r.

Data given in Table 3 show that the suggested hypothesis is probable.

Table 3

Dependence of r of precipitated TiO_2 (in m) on the filling degree. D (Gy) = 150

Filling degree, kg/m^3	10^6 r of precipitated particles	
	control	irradiated
10	155	163
20	160	195
30	180	226
40	190	290

3.3. Influence of Radiation on Some Properties of Fillers Used in Epoxy Glues

The surface state of F is one of the most important factors which ensures the receipt of filled PM with performed properties.

From this point of view it is important to know the nature and the strength of intermolecular interactions which occur in the system including heterogeneous processes. The SP modification plays an important role under this treatment which is discussed in detail.

The recipes of epoxy composites, in particular glues, apart binding agents and hardeners also include fillers, accelerants, plasticizers, and so on.

To carry out systematic investigations model systems must be studied at first. To create such systems the number of components must be reduced to minimum.

The results concerning the study of some epoxy glues which contain linking (bonding) compounds ED-20, hardener L-20 and F will be discussed below.

3.3.1. Interaction of SiO_2 with ED-20 and L-20 [23]

The used SiO_2 samples are the same. There are not principal differences in their behaviour. L-20 and ED-20 adsorption dependences on D may the expressed by curves which pass through extremum: maximum in the case of L-20 and minimum in the case of ED-20. In both cases extremum values of Ad correspond to $D_{ex} \cong 150$ Gy.

It is obvious that the main acting factor is the nature of the hydrate-hydroxyl cover on SiO_2 particles surface. It is shown that concentration changes of both epoxy

and hydroxy (OH) groups occur in systems which consist of mixtures F+ED-20 or F+L-20.

Apart from completion of experiments with cited oligomers it is established, that the mean value of molecular mass (M_n) of the used oligomers in the solution increased.

This shows that macromolecules with less molecular masses participate mainly in surface reactions, because they are mobile and have more linear structure. To generalize the stated regularities apart from SiO_2, other solid oxides as fillers are studied too (see Fig. 2 and Table 4).

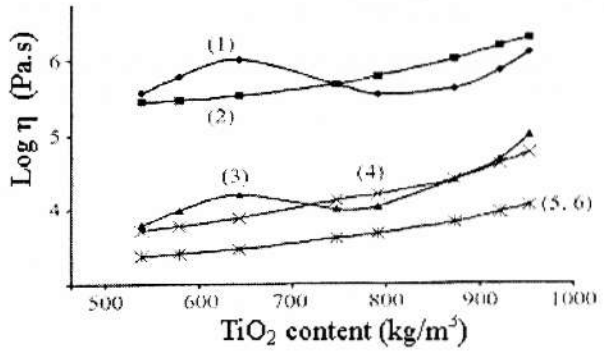

Fig. 2. L-20 adsorption (Ad) dependence on D on SiO_2 (1), TiO (2) and talc (3)

Table 4

ED-20 adsorption on SiO_2 and Al_2O_3
(initial ED-20/benzene solution is 7mas %, adsorption time is 2 days)

D, Gy	Adsorption 10^3, kg/kg	
	SiO_2	Al_2O_3
Control	120	10.0
50	75	7.5
150	60	6.6
150	60	6.2
200	62	7.0
300	70	8.0

In the case of L-20 adsorption there is a maximum, while in the case of ED-20 there is a minimum on Ad–D curves. This regularity does not depend on the fillers nature. This circumstance provokes the necessity to pay attention to the sequence of components addition for obtaining glue composite.

From our data it follows that the best glue composite may be obtained when ED-20 is added to the F+L-20 mixture.

The study of the hardening kinetics of prepared glue composite and tensile strength measuring of gluing together proves the rightness of the made conclusion.

4. Conclusions

For the first time the possibility of fillers surface properties (SP) modification exposed to the action of penetrating radiation of small doses (D) (approximately of the 100 Gy order) has been shown. The influence of preliminary irradiation (X-rays, gamma) of some mineral powders (SiO_2, MgO, TiO_2, ZnO, talc, kaolin) on their adsorption, suspensions, rheologic properties and behaviour in the presence of some additions has been studied. It has been established that oxides SP dependence in the absence and in the presence of different additions on irradiation D is described by the curves with extremums. They correspond to D_{max} of the 100 Gy (10000 rads) order.

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ХАРАКТЕРИСТИКА ДЕЯКИХ ОПРОМІНЕНИХ ТВЕРДИХ ОКСИДІВ У РІЗНИХ СЕРЕДОВИЩАХ І В ПРИСУТНОСТІ ДОДАТКІВ

Анотація. *Властивості наповнених полімерних клейових композицій значною мірою залежать від природи і поверхневих властивостей наповнювачів, зокрема, твердих оксидів. Вперше показано можливість модифікації поверхневих властивостей твердих оксидів невеликими дозами проникної радіації (≈ 10^2 Gy). Вивчено вплив попереднього опромінювання (Х-опромінення, гама-промені) деяких мінеральних порошків (SiO_2, MgO, TiO_2, ZnO, тальк, каолін) на їх адсорбційні та реологічні властивості і їх поведінку у присутності певних додатків. Встановлена залежність поверхневих властивостей оксидів від опромінення у присутності і без додатків, яка має екстремальний характер. Показано, що максимум відповідає опроміненню порядка 10^2 Gy.*

Ключові слова: *полімерні клейові композиції, наповнювач, гамма-випромінення, Х-промені.*