Acid-basic surface properties of dispersed fillers based on metal oxides TiO$_2$, Al$_2$O$_3$, CaO and Fe$_2$O$_3$

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Abstract. The dispersed oxide fillers of different chemical composition were investigated: rutile (TiO$_2$), alumina (Al$_2$O$_3$), calcite (CaO) and hematite (Fe$_2$O$_3$). The mineral composition, surface morphology, particle size and specific surface of the fillers were investigated using modern physicochemical methods. It has been established that the acid-alkaline properties of the active surface centers (ASC) and hydroxyl-hydrate layer (HHL) depend on the chemical and mineral nature of the fillers. It is established that with decreasing acidity of the oxide, the desire for its surface to adsorb water molecules from the air increases. As the alkalinity of the oxide increases, the thickness of both the hydroxyl and hydrate surface layers increases in proportion. It is shown that the acid-alkaline properties of the surface correlate with the acid-alkaline properties of the oxides included in the fillers.

1. Introduction and literature review

Oxide dispersive fillers are widely used for the development of new effective polymeric building and restoration composite materials. Metal oxide-based fillers are added to composites to reduce costs and increase the environmental friendliness of materials. By adding oxide fillers, it is possible to adjust the technological properties of the polymer composites, to improve the physical and mechanical characteristics and to give special properties of the materials for certain operating conditions [1-4]. Disperse oxide fillers of different chemical nature can give materials special properties (resistance to biologically and chemically corrosive media, resistance to radiation, fire resistance, vibration-absorbing properties) [5-9]. At the same time, the addition of oxide fillers ensures the production of polymeric materials with certain decorative properties, which is important when used in design, architecture and restoration [10, 11]. For composite polymeric materials, dispersed fillers based on Al$_2$O$_3$, Fe$_2$O$_3$, Cr$_2$O$_3$, TiO$_2$, FeO, ZnO, CaO, MgO, BeO, BaO, CuO provide regulation of technological and operational properties over a wide range [12-15]. It is believed that the regulation of the properties of the materials is associated with the completeness of contact adhesion and wetting on the boundary between the phases in the “polymer-filler” system. In the study of these processes, the nature and properties of the surface of the oxides are hardly taken into account.

The influence of the surface of the dispersed fillers on the properties of the filled polymeric materials plays a crucial role in obtaining multifunctional composites with improved performance. This is due to the processes and surface phenomena occurring at the boundary of the "polymer-filler" phase separation. The properties of the surface layer of the fillers determine the physicochemical processes occurring at the interfacial boundary - adsorption, wetting, polymer flow on the surface of
the filler, the formation of the interfacial layer, impregnation, the phenomenon of capillaries, as well as the formation of physico-chemical, possibly chemical bonds. There is currently no consensus on the mechanism of interfacial interaction. It would be a mistake to say that all of these processes occur by the same mechanism. Therefore, the study of the mechanisms of interfacial interactions requires careful examination and study of every possible theory. One of the least studied theories of interfacial interaction is acid-base, which has been the subject of research in recent years [4, 6, 8]. The existence of acid-base interfacial interactions is based on the following facts. Polymeric binders have a number of functional groups that can enter into acid-base reactions according to Lewis or Brønsted. For example, OH-groups formed in large numbers during the cross linking process of epoxyamine mesh polymers can act as Brønsted acids or bases [4]. Oxygen O:, nitrogen N:, and sulfur S: atoms with an undivided free electron pair act as Lewis bases. A carbon atom can, under certain conditions, act as a Lewis acid. The surface of inorganic fillers, namely metal oxides, may contain OH-groups related to Brønsted [5, 6]. On the surface of the oxides, the oxygen atom acts as a Lewis base, and the free-orbit Me\(^+\) metal atom acts as a Lewis acid. In figure 1 presents a possible acid-base mechanism (Lewis and Brønsted) interfacial interaction between calcium oxide and epoxyamine polymer. It should be noted that acid-base reactions occur in the filled composites at the phase boundary, which are most likely not chemical, but end at the level of weak low-energy interactions.

![Acid-base interaction](image1)

**Figure 1.** Acid-base mechanism (Lewis and Brønsted) of the interfacial interaction between calcium oxide and the epoxyamine polymer.

The information on the acid-basic properties of the functional groups of the polymer and the active surface centers (ASC) on the fillers creates the preconditions for predicting the acid-base interactions on the interfacial surface and allows directional selection of constituent composite materials.

On the surface of inorganic fillers there is a hydroxyl-hydrated layer (HHL), which consists of functional different chemical nature with a wide range of acid-basic characteristics. With the use of quantum-chemical modeling, models of anhydrous and hydrated centers on the surface of inorganic fillers based on CaO, MgO, FeO, Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), SiO\(_2\), TiO\(_2\) oxides are proposed [16]. The created chemical structural formulas of the centers take into account the chemical nature, the crystalline structure, the aggregate state and the conditions for the flow of surface equilibrium processes. It has been established that the acidity values of pK\(_a\) of all anhydrous centers have high values from 7.9 to 16.9. Accordingly, the Gibbs free energy value of deprotonation of the centers is positive and varies from 45.4 to 96.4 kJ/mol. It is shown that the acidity of isolated and vicinal centers is directly proportional with increasing the number of OH-groups and adsorbed water molecules. The method of quantum-chemical modeling of molecular systems and experimental rheological studies have shown that in epoxy polymers with inorganic fillers, interfacial processes occur by acid-base reactions and with the direct participation of weakly acidic OH-groups of the polymer [4]. As a result of the theoretical and experimental study, regularities of the influence of the acid-base properties of the surface of inorganic fillers on all stages of the formation of filled epoxy polymeric composite materials have been established: at the stage of the structure of the epoxy resin in the viscous-liquid
state, at the stage of the chemical reaction of the cross linking in the transition to the vitreous state and the stage of formation of the spatial orientation of a polymer mesh in vitreous state [2]. It is shown that the influence of fillers on the structure and spatial conformation of the epoxy grid depends on the surface acid-base properties and increases with the increase of the alkalinity of the oxide. With certain alkaline properties of oxide, the spatial conformation of the epoxy grid is substantially changed as a result of strong hydrogen and donor-acceptor bonds. It has been found that in order to obtain composites with improved technological and operational properties, it is necessary to use fillers with a weakly acidic or weakly basic surface function and high general concentration of Brønsted and Lewis groups.

It is known that HHL forms on the surface of inorganic materials as a result of chemical and physico-chemical adsorption of water molecules on surface OH-groups with excess surface energy [17]. The number of water molecules and the mechanism of adsorption affect the acid-base characteristics of HHL [6, 16]. It has been proved that acid-base parameters of ASC change during burning or machining [18]. The structure and acid-base properties of the surface layer of clay fillers were studied in [6]. There is no such study for oxide materials. Therefore, the subject of this study is the experimental study of the characteristics and properties of HHL of fillers based on oxides of TiO$_2$, Al$_2$O$_3$, CaO, Fe$_2$O$_3$.

The HHL on surface of oxide materials consists of two main parts - the first hydroxyl (chemically bonded water molecules forming the OH-group with a wide range of acidity) and the second hydrate (bonded water molecules with the previous hydroxyl layer due to hydrogen bonds and low energy physico-chemical bonds). In chemical structure and acid-base characteristics, a wide range of ACS is present on the surface, which may contain different amounts of Me$^{+\#}$ metal atoms, oxygen atoms O: , hydroxyl OH-groups and H$_2$O water molecules [16]. Due to the unspecified structure, the study of the acid-base properties of ASC is a complex scientific task. For this purpose, theoretical and experimental methods are used - quantum chemical modeling, IR-spectroscopy, adsorption of gas molecules and color indicators, potentiometric method [6, 19-21].

Thus, in view of the above, the aim of this study is to experimentally investigate the acid-base properties of the HHL surface of oxide materials, which are most common for filling polymer composites. It is also interesting to explore the relationship between the chemical, mineral structure of fillers and the properties of HHL.

2. Materials and methods of research
The oxide fillers of various chemical and mineral compositions were selected as research materials: rutile (TiO$_2$), alumina (Al$_2$O$_3$), calcite (CaO) and hematite (Fe$_2$O$_3$). The mineral composition of the fillers was investigated on an X-ray diffractometer DRON-2 (Russia). Particle size and surface morphology were determined using a JSM-6390LV scanning electron microscope (Japan). The specific surface was determined by the BET method (Brunauer, Emmett and Teller). For the HHL study, thermogravimetric (TG) analysis and differential thermal analysis (DTA) were used using SDT Q600 and Instruments (USA). Two physicochemical experimental methods were used to investigate the acid-base properties fillers: pK-metric and pH-metric.

The pK metric method is designed to quantify ASC with certain acidity and is based on the adsorption of Gamete color indicators from aqueous solutions in suspensions. To obtain information on the number ASC as large as possible, 14 color indicators with a pK (negative logarithm of the acid dissociation constant of the indicator) from −0.29 to +12.8 were used. Based on the results obtained, the following informative indicators are calculated: $\Sigma qA$ is the sum of the number of acidic ASCs observed in the adsorption of color indicators with pK<7; $\Sigma qB$ is the sum of the number of alkaline ASCs observed in the adsorption of color indicators with pK>7; $\Sigma q = \Sigma qA + \Sigma qB$ is the total number of ASCs on the filler surface; $Q = \Sigma qA / \Sigma qB$ is an integral indicator that makes it possible to evaluate the surface in general as neutral ($Q \approx 1$), acidic ($Q > 1$) or basic ($Q < 1$).

The pK-metric method is sufficiently informative and capable of providing some quantitative and qualitative characteristics of ASC, but does not provide an opportunity to evaluate the properties of HHL. The method has been successfully used to study the properties of inorganic dispersed materials of various chemical and mineral nature [6, 8, 19].
The pH-metric method is intended for the integral evaluation of the acid-base properties of the surface layer HHL of dispersed materials and is based on the measurement of pH\(_{\text{susp}}\) of aqueous suspensions of fillers in the process of establishing equilibrium. The pH\(_{\text{susp}}\) was measured by a potentiometric method. According to the results obtained, the following informative indicators were determined and calculated: pH\(_{\text{eq}}\)\(_{\text{susp}}\) is pH\(_{\text{susp}}\) value in equilibrium state (at the time of setting constant pH\(_{\text{susp}}\) value); pH\(_{\text{HILP}}\) = pH\(_{0}\) + (pH\(_{\text{eq}}\)\(_{\text{susp}}\) − pH\(_{0}\)) \cdot (pH\(_{0}\) − 6) is pH\(_{\text{susp}}\) value of the isoadsorption point (zero charge point), at which no mass transfer of ions from the solution to the surface of the solid occurs; \(\Delta\text{pH} = \text{pH}_{\text{HILP}} - \text{pH}_{\text{eq}}\)\(_{\text{susp}}\) is an indicator that indicates the width of the ASC band on the surface of the filler; \(\tau^{eq}\) is an indicator that characterizes the length of time the equilibrium is established in the suspension.

The pH-metric method allows evaluating the integral acid-base characteristic of the filler surface, to estimate the ASC spectrum and to obtain information on the structure and nature of HHL.

3. Study of mineral composition, size particles and surface area of oxide fillers

The results of the study of mineral composition, size particles and surface area of oxide fillers are presented in table 1 and on figures 2-5.

| Filler         | Mineral composition                                | Surface area (m\(^2\)/g) | Preferred particle size (\(\mu\)m) |
|----------------|---------------------------------------------------|---------------------------|-----------------------------------|
| Rutile (RT)    | Rutile (TiO\(_2\))\(^•\)                         | 1.30                      | 5-10                              |
|                | Anatase (TiO\(_2\))\(^•\)                        |                           |                                    |
| Alumina (AM)   | Corundum (\(\alpha\)-Al\(_2\)O\(_3\))\(^•\)      | 20.00                     | 20-50                             |
|                | Alumina (\(\gamma\)-Al\(_2\)O\(_3\))\(^•\)       |                           |                                    |
| Calcite (CT)   | Calcite (CaCO\(_3\))\(^•\)                      | 7.95                      | 25-30                             |
|                | Hematite (\(\alpha\)-Fe\(_2\)O\(_3\))\(^•\)      |                           |                                    |
|                | Goethite (FeOOH)\(^•\)                           |                           |                                    |
|                | Limonite (Fe\(_2\)O\(_3\)\_H\(_2\)O)\(^+\)       |                           |                                    |
| Hematite (HT)  | Calcium aluminoferrite (4CaO\_Al\(_2\)O\(_3\)_Fe\(_2\)O\(_3\))\(^+\) | 11.35                     | 1.5-3                             |
|                | Ettlingite (3CaO\_Al\(_2\)O\(_3\)_3CaSO\(_4\)_3H\(_2\)O)\(^+\) |                           |                                    |

**Table 1. Properties of oxide disperse fillers.**

Remarks: • – basic mineral phase; + - side mineral phase.

Alumina (AM) \(\gamma\)-Al\(_2\)O\(_3\), a white powder, is obtained from natural bauxites by the hydrochemical method or by the method of sintering. It is used for the production of ceramics, glass, anticorrosive coatings. Microphotographs show spherulites of size 20-50 \(\mu\)m, characteristic of \(\gamma\)-Al\(_2\)O\(_3\). With an increase of 2000 it is evident that the spherulites are formed from grains of scaly form. This indicates the modification transition \(\gamma\)-Al\(_2\)O\(_3\) \(\rightarrow\) \(\alpha\)-Al\(_2\)O\(_3\). Grain surface without pores and no defects (Figure 2). No admixtures are observed, which is confirmed by an X-ray, where peaks exist that correspond to \(\gamma\)- and \(\alpha\)-modifications of aluminum oxide. Rutile (RT) is a powder of red-brown color, a product of crushing the rutile mineral of the chemical formula TiO\(_2\). As accompanying minerals, \(\beta\)-quartz SiO\(_2\) and ilmenite of the general chemical formula FeO\_TiO\(_2\) or FeTiO\(_3\) may be used. According to the results of X-ray diffraction analysis, the powder is mostly represented by rutile. In the smaller number there is anatase. The powder is strongly agglomerated. Agglomerates consist of dense grains in the size of 1-2 \(\mu\)m. Agglomerates have a predominant size of 5-10 \(\mu\)m (Figure 3). Calcite (CT) is a white powder, lime spat is a CaCO\(_3\) mineral from a group of carbonates, one of the natural forms of calcium carbonate. Calcite is represented by dense particles of an isometric shape of a predominant dispersion of 25-30 \(\mu\)m. In small quantities there is grain size 50-60 \(\mu\)m. With an increase of 3000-10000 visible single inclusion of the phase of white color. The plane of cleavage of calcite crystals is clearly visible. The surface of the grains is well developed, uneven (Figure 4).
Figure 2. Microphotographs for rutile (RT).

Figure 3. Microphotographs for alumina (AM).
Figure 4. Microphotographs for calcite (CT).

Figure 5. Microphotographs for hematite (HT).
Hematite (HT) is a disperse powder of red-brown color, wastes of alumina production. On the diffractogram there is a set of blurry diffraction maxima of weak intensity corresponding to hematite $\alpha$-$\text{Fe}_2\text{O}_3$ and FeOH goethite. In the form of impurities in the powder there is lemonite $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, four-calcium aluminoferrite $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ and ettringyte $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$. The predominant dispersion of red mud is 1.5-3 µm. There are large particles in the size of 4-5 µm. With an increase of 20000 to 300000, it is evident that the powder is sufficiently homogeneous, the grains are dense, non-porous and isometric (Figure 5).

4. Study of the dynamics of mass loss of oxide fillers

In table 2 shows the dynamics of mass loss of oxide fillers in the process of increasing temperature.

| Filler      | Weight loss of the filler in the temperature range (%) |
|-------------|-------------------------------------------------------|
|             | 0-150°C | 150-300°C | 300-600°C | 600-900°C |
| Rutile (RT) | 0.4     | 0.2       | 0.3       | 0.2       |
| Alumina (AM)| 0.3     | 1.0       | 0.6       | 0.5       |
| Calcite (CT)| 0.0     | 0.0       | 0.0       | 42.5      |
| Hematite (HT)| 2.5   | 3.7       | 3.1       | 3.8       |

From the results presented in the table 2 it is possible to draw the following conclusions. At temperatures from 0-300 °C, dehydration processes occur, that is, the loss of physically adsorbed on the surface of water molecules (the hydrated layer). At temperatures from 300-900°C, dehydroxylation processes occur, that is, the loss of chemosorbed water molecules (hydroxyl layer). Thus, the thickness of the hydrated surface layer of fillers increases in a row:

$$\text{CT (0.0%)} < \text{RT (0.6%)} < \text{AM (1.3%)} < \text{HT (6.2%)}. \quad (1)$$

The thickness of the hydroxyl layer of fillers increases in a row:

$$\text{CT (0.0%)} < \text{RT (0.5%)} < \text{AM (1.1%)} < \text{HT (6.9%)}. \quad (2)$$

From the series obtained, we can draw the following conclusions. Chemically and physically bound water was not detected on the surface of calcite by a thermal method. The loss of mass in the range 650-710 °C is obviously due to the removal of CO$_2$ carbon dioxide present in calcite. In rutile, alumina and hematite, the thickness of the hydrated surface layers (1) correlates with the thickness of the hydroxyl layers (2). In this case, the surface of HT is characterized by the largest thickness of the HHL.

5. Study of pK-metric and pH-metric methods for oxide fillers

The results of pK-metric and pH-metric experimental studies of oxide fillers are presented in table 3 and table 4.

| Filler     | $\sum q_A \cdot 10^{-14}$ (1/cm$^2$) | $\sum q_B \cdot 10^{-14}$ (1/cm$^2$) | $\sum q \cdot 10^{-12}$ (1/cm$^2$) | Q       |
|------------|-------------------------------------|-------------------------------------|-------------------------------------|---------|
| Rutile (RT)| 73.18                               | 95.84                               | 169.02                              | 0.76    |
| Alumina (AM)| 8.47                               | 14.05                               | 22.55                               | 0.60    |
| Calcite (CT)| 10.06                              | 42.96                               | 53.02                               | 0.23    |
| Hematite (HT)| 25.89                              | 67.05                               | 92.98                               | 0.39    |

From table 3 it follows that the acidity of the surface of oxide fillers depends significantly on the mineral composition and nature of the oxide. Considering the results of the pK-metric analysis, it should be noted that the relatively homogeneous mineral composition of the fillers does not guarantee the formation of the same type of active centers on the surface. For example, on the RT surface, the composition of which is represented by rutile, acidic centers with pK$_a$ = -0.29-5.0 were found to be about 30%, alkaline with pK$_a$ ≈ 8.8-12.8 about 50% and neutral about 20%. A large number of
alkaline and strongly alkaline centers cause the general weakly alkaline, closer to the neutral, the nature of the surface RT (Q ≈ 0.76). A wide spectrum of the function of acidity of centers on the RT surface is due to the formation of various types of isolated and vicinal centers, which differ in the number of OH-groups and adsorbed water molecules. As previously shown [22], an increase in OH-groups in the active center increases acidity. A wide range of RT surface centers results in a relatively long period of equilibrium setting in aqueous suspension (360 s).

| Filler       | pHₜ for distilled water | pHₜsup | pHₜIP | ΔpH  | teq (s) |
|--------------|-------------------------|--------|-------|------|---------|
| Rutile (RT)  | 7.50                    | 8.16   | 8.49  | 0.33 | 360     |
| Alumina (AM) | 7.25                    | 9.05   | 9.50  | 0.45 | 120     |
| Calcite (CT) | 7.30                    | 9.42   | 10.06 | 0.64 | 420     |
| Hematite (HT)| 8.00                    | 9.70   | 11.40 | 1.71 | 420     |

Polymineral composition of HT obviously causes the detection of acidic centers with pKₐ ≈ -0.29-5.0 about 25%, alkaline with pKₐ ≈ 8.8-12.8 about 70% and neutral about 5%. The vast majority of alkaline and strongly alkaline centers cause a strongly alkaline general nature of the surface HT (Q ≈ 0.39). A wide spectrum of surface centers with the opposite function is confirmed by the large values of ΔpH = 1.71 and the time of establishing the equilibrium state in an aqueous suspension of 420 s. The results of the pK-metric analysis revealed an identical character of the spectrum of the acid-base active centers on the CT and AM surfaces. On the surface of both fillers there are alkaline centers with pKₐ = 9.5-11.5 in the amount of 92-98% and a small number of acid and neutral centers. This causes a strongly alkaline nature of the surface CT (Q ≈ 0.23) and the alkaline nature of the surface AM (Q ≈ 0.60). On the CT surface, 2.5 times the total number of active centers was detected than on the AM surface. This is confirmed by a greater than 3 times the time of equilibrium in suspensions: CT - 420 s, AM - 120 s. In addition, this can be explained by three times the total alkaline nature of the surface of the CT.

Thus, according to the results of pK-metric analysis (Table III), the alkalinity of oxide fillers increases in a number:

RT (Q ≈ 0.76) < AM (Q ≈ 0.60) < HT (Q ≈ 0.39) < CT (Q ≈ 0.23).  

(3)

According to the results of the potentiometric analysis (table 4), the alkalinity of the surface of the oxide fillers, in accordance with the value of pHIP, increases in the series:

RT (8.16) < AM (9.50) < CT (10.06) < HT (11.40).  

(4)

According to the theoretical calculations on the basis of quantum-chemical modeling [20], the alkalinity of active centers on the surface of oxides increases in the series:

TiO₂ < Al₂O₃ < Fe₂O₃ < FeO < CaO.  

(5)

The comparative characteristic of the obtained series (3), (4) and (5) allows us to confirm the unconditional correlation found between the experimentally determined acid-base properties and the theoretical calculation. The exception is a larger theoretically calculated alkalinity of CaO active centers. This, obviously, is due to the fact that the calculation does not take into account the presence of acid CO₂ in the composition of calcite CaCO₃, which reduces the alkalinity of the surface of the CT. If we exclude CT from the list of studied fillers, one can see the correlation between the acid-base surface properties, the alkalinity of the oxides that are part of it, and the thickness of the hydroxyl-hydrated surface layer of fillers. Therefore the acid-base surface properties of oxide fillers will be determined not by the number of adsorbed water molecules on the surface, but by the chemical and mineral nature of the oxides. On the other hand, it is interesting that with decreasing acidity of oxides, the desire for adsorption on the surface of water molecules increases. This is evidenced by the increase in the thickness of both the hydroxyl and hydrate layers.
6. Conclusions
The results of the study allow us to formulate several conclusions. Mineral composition, surface morphology, particle size and specific surface area were determined for the most commonly used fillers polymeric composites of rutile (TiO₂), alumina (Al₂O₃), calcite (CaO) and hematite (Fe₂O₃). The structure of the surface HHL of the fillers was studied using thermogravimetric (TG) analysis and differential thermal analysis (DTA). The quantity and acid strength of active surface centers (ASC) fillers were investigated by the methods of pK-metric and pH-metric. It is established that the acid-basic properties of ASC and hydroxyl-hydrated layer (HHL) in general depend on the chemical and mineral nature of the fillers. It is established that with decreasing acidity of the oxide the desire of its surface for adsorption of water molecules increases. In this case, the thickness of both the hydroxyl and hydrated surface layers increases proportionally. Studies have shown that acid-base surface properties correlate with acid-base properties of oxides that are part of fillers.

Acknowledgements
The authors are grateful to Dr. Sergey U. Sayenko from the Institute of Solid State Physics, Materials Science and Technologies NAS of Ukraine and Olexandr S. Bakevich from the Ukrainian State University of Chemical Technology for assistance in conducting the experiment. The work is supported by the Ministry of Education and Science of Ukraine (State registration number 0114 U 004376).

References
[1] Wypych G 2016 Handbook of Fillers (ChemTec Publishing)
[2] Danchenko Yu, Andronov V, Barabash E, Obigenko T, Rybka E, Meleshchenko R and Romin A 2017 Research of the intramolecular interactions and structure in epoxymine composites with dispersed oxides East.-Europ. J. of Ent. Tech. 6 12 (90) 4-12
[3] Pozdzieiev S, Pidgoretskiy Y, Nekora O, Sidnei S and Tyschchenko O 2018 Research of explode exposure at the relief vent system structures with soft transparent material Intern. J. of Eng. and Tech. (UAE) 7 (4.3) 3 298-302
[4] Danchenko Yu, Kachomanova M and Barabash Ye 2018 The acid-base interaction role in the processes of the filled diene epoxy resin structuring Chem. & Chem. Tech. 12(2) 188-195
[5] Fei-Zhou Li, Zheng-Lin Lu, Zhi-Huai Yang and Kai Qi 2015 Surface interaction energy of ceramic materials with epoxy resin Polimery 60(7-8) 468-471
[6] Danchenko Yu, Andronov V, Sopov V, Khmyrov I and Khryapynskyy A 2018 Acid-basic surface properties of clay disperse fillers MATEC Web of Conf. 230
[7] Skripinets A, Danchenyk Y and Kabush' A 2015 A research on technological and physicochemical laws of manufacturing vibration-absorbing products based on epoxy-urethane polymer compositions. East.-Europ. J. of Ent. Tech. 3(11) 4-8
[8] Danchenko Y, Andronov V, Obizhenko T, Kosse A and Khmyrov I 2018 The influence of inorganic fillers on the protective properties of epoxy polymer composite materials Intern. J. of Eng. and Tech. (UAE) 7(4.3) 3 279-283
[9] Sainenko N, Demidov D, Popov Y, Bikov R and Butskyi V 2018 Rheological properties of aqueous dispersion of styrene acrylate copolymer incorporating hollow microspheres and AEROSIL® MATEC Web of Conf. 230
[10] Cardiano P, Ponterio R C, Sergi S, Lo Schiavo S and Piraino P 2005 Epoxy-silica hybrids as stone conservation materials Polymer 46(6) 1857-1864
[11] Karayannidou E G, Achillas D S and Sideridou I D 2006 Cure kinetics of epoxy-amine resins used in the restoration of works of art from glass or ceramic Europ. Polym. J. 42(12) 3311-3323
[12] Dasari A, Yu Z Z, Cai G P and Mai Y-W 2013 Resent developments in the fire retardancy of polymeric materials Prog. Polym. Sci. 38 1357-1387
[13] Rui Li, Haoruo Zhang, Cheng Zhou, Bin Zhang, Yang Chen, Huawei Zow and Mei Liang 2017 The thermal stability investigation of microencapsulated ammonium polyphosphate/siloxane – modified epoxy resin composites J. of Appl. Polym. Sci. 134(36) 45272-45280
[14] Fu Y-X, He Z-X and Mo D-C 2014 Thermal conductivity enhancement with different fillers for epoxy resin Adhesives Appl. Therm. 66 493-498
[15] Saienko N V, Demidov D V, Popov Y V, Bikov R A, Yunis B and Saienko L V 2019 Effect of mineral filler compounds on vapor permeability and hydroscopic properties of water-based polymer dispersions Mater. Sci. Forum. 968 89-95
[16] Danchenko Yu, Andronov V, Rybka E and Skliarov S 2017 Investigation into acid-basic equilibrium on the surface of oxides with various chemical nature East.-Europ. J. of Ent. Tech. 4 12(88) 17-25
[17] Miller C M 2010 Adhesion and the surface energy components of natural minerals and aggregates (Submitted to the Office of Graduate Studies of Texas A&M University in partial fulfillment of the requirement for the degree of Master of Science)
[18] Zapata-Massot C and Le Boley N 2007 Effect of the mineral filler on the surface properties of co-ground polymeric composites Part. Part. Char. 24 339-344
[19] Weissenbach K and Mack H 2005 Silane coupling agents, Functional Fillers for Plastics, (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) 59-83
[20] Melnyk L, Bessarab O, Matko S and Malyovanyy M 2015 Adsorption of heavy metals ions from liquid media by palygorskite Chem. & Chem. Tech. 9(4) 467-470
[21] Malyovanyy M, Sakalova G, Chornomaz N and Nahurskyy O 2013 Water sorption purification from ammonium pollution Chem. & Chem. Tech. 7(3) 355-358
[22] Danchenko Yu, Andronov V, Teslenko M, Permiakov V, Rybka E, Meleshchenko R and Kosse A 2018 Study of the free surface energy of epoxy composites using an automated measurement system. East.-Europ. J. of Ent. Tech. 1 12(91) 9-17