ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 5, pp. 810–815. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © P.A. Sitnikov, A.V. Kuchin, M.A. Ryazanov, A.G. Belykh, I.N. Vaseneva, M.S. Fedoseev, V.V. Tereshatov, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 5, pp. 717–722.

Influence of Acid-Base Properties of Oxides Surface on Their Reactivity Towards Epoxy Compounds

P. A. Sitnikov[a], A. V. Kuchin[a], M. A. Ryazanov[a], A. G. Belykh[a], I. N. Vaseneva[a], M. S. Fedoseev[b], and V. V. Tereshatov[b]

[a] *Institute of Chemistry, Komi Scientific Center, Ural Branch, Russian Academy of Sciences,*
ul. Pervomaiskaya 48, Syktyvkar, 167000 Russia
e-mail: sitnikov-pa@chemi.komisc.ru

[b] *Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences, Perm, Russia*

Received July 22, 2013

Abstract—Acid-base properties of surface of aluminum, iron, and silicon oxides have been studied by p*K* spectroscopy. γ-Al_2O_3 and γ-AlO(OH) have been found the most reactive modifiers for epoxy oligomers, due to the presence of active surface groups with $pK_1 \approx 4$, capable of chemical interaction with the matrix.

Keywords: metal oxide, epoxide, polymer, reactive filler, equilibrium constant, homopolymerization

DOI: 10.1134/S107036321405003X

Active fillers can significantly alter utilitarian properties (mechanical strength, thermal or heat resistance, and electrical conductivity) of polymeric epoxide-based materials due to formation of interphase adsorption layer at the polymer–filler boundary [1]. To date, no unified approach to estimate, predict, and regulate the interactions at the interphase boundary has been developed [2].

Almost any natural or synthetic material can act as filler for polymer material, including the polymers themselves, after certain modification of their surface. Proper selection of the polymer and filler combination should account for the filler nature, particles shape and size, its distribution in the matrix as well as possible interactions with the polymer at the interphase boundary. Chemical reactivity of the filler surface (that is in turn determined by its functional composition) is of particular importance [1, 2].

Metal oxides are widely used as fillers for thermoplasts and thermosetting plastics. In particular, in this work we studied well known [3–7] silicon oxide (aerosil) and various modifications of aluminum oxide [γ-AlO(OH), γ-Al_2O_3, α-Al_2O_3] and iron(III) oxide [γ-FeO(OH), γ-Fe_2O_3, α-Fe_2O_3] in order to elucidate the effect of acid-basic properties of the oxides surface on physico-chemical processed taking place upon the oxides incorporation into epoxy compounds.

The most widely used method to investigate the acid-base (Brønsted–Lowry) properties of metal oxide materials is potentiometric titration of the suspensions in aqueous medium. The acid-base properties can be conveniently represented by p*K* spectra [8], by plotting the fraction of the acid-base sites with the corresponding p*K* (or their specific concentration *q*, mmol/g) as function of p*K*. p*K* spectra can be obtained from potentiometric titration curves.

$$G_n(pH) = n_b(pH) + n_H^0 = \frac{c_{HA}V_0 - c_{BOH}V - [H^+](V_0 + V)}{m} + n_H^0.$$

In the equation above: n_H^0, amount of hydrogen ions (mmol/g) adsorbed at the suspension particles at the starting point of titration pH_0; n_b(pH), amount of hydrogen ions (mmol/g) adsorbed at the suspension particles in the course of titration to the current pH; V_0, suspension volume; c_{HA}, concentration of monobasic strong acid in the suspension; V, volume of the added alkali with concentration of c_{BOH};

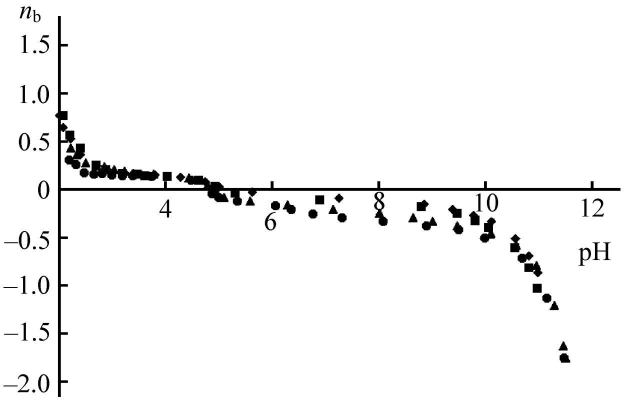


Fig. 1. Adsorption of hydrogen ions at Al_2O_3 surface as function of pH. (Diamonds) 1st direct titration; (squares) 2nd direct titration; (triangles) 1st back titration; and (circles) 2nd back titration.

m, mass of the solid phase of the suspension in the sample.

Acid-base properties of oxide materials can be interpreted taking advantage either of the 2p*K* or the 4p*K* model [9].

The 2p*K* model is based on the assumption that the surface charge appears via ionization of amphoteric groups –S–OH, [Eqs. (1) and (2)] (hereafter S stands for the sample surface).

$$-\text{S–OH}_2^+ \rightleftarrows -\text{S–OH} + \text{H}^+,\ K_1 = \frac{\text{SOH}][\text{H}^+]}{[-\text{SOH}_2^+]}, \tag{1}$$

$$-\text{S–OH} \rightleftarrows -\text{S–O}^- + \text{H}^+,\ K_2 = \frac{[-\text{SO}^-][\text{H}^+]}{[-\text{SOH}]}. \tag{2}$$

The equilibrium constants K_1 and K_2, being independent of the background electrolyte concentration, characterize the acid-base sites strength.

In the acidic medium, the surface charge is predominantly determined by equilibrium (1), whereas in the alkaline media the equilibrium (2) is far more important.

The 4p*K* model accounts for further reactions involving the background electrolyte, in particular, partial neutralization of surface charge with its ions. For example, ion pairs formation involving NaCl is described by Eqs. (3) and (4).

$$-\text{S–OH}_2^+\text{Cl}^- \rightleftarrows -\text{S–OH} + \text{H}^+ + \text{Cl}^-,$$

$$K_3 = \frac{[\text{SOH}][\text{H}^+][\text{Cl}^-]}{[\text{SOH}_2^+\text{Cl}^-]}, \tag{3}$$

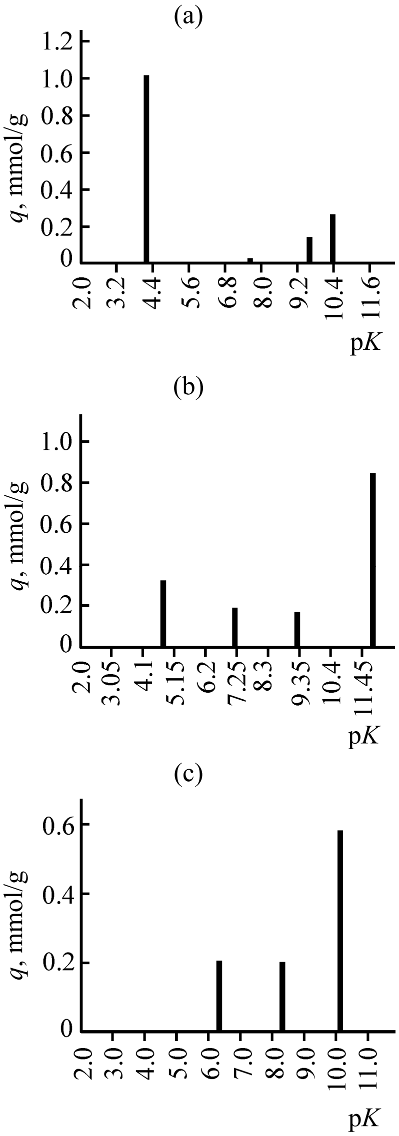


Fig. 2. pK spectra of γ-AlO(OH) (a), γ-Al_2O_3 (b), and α-Al_2O_3 (c).

$$-\text{S–OH} + \text{Na}^+ \rightleftarrows -\text{S–O}^-\text{Na}^+ + \text{H}^+,$$

$$K_4 = \frac{[\text{SO}^-\text{Na}^+][\text{H}^+]}{[\text{SOH}][\text{Na}^+]}. \tag{4}$$

The high K_3 and K_4 values point at specific adsorption of cations, whereas low values of the constants reflect specific adsorption of anions [8].

Typical plots of n_b(pH) recalculated from direct and back titration curves are shown in Fig. 1 taking γ-Al_2O_3 as a representative example. As the results of sequential titrations were identical, the studied processes were reversible.

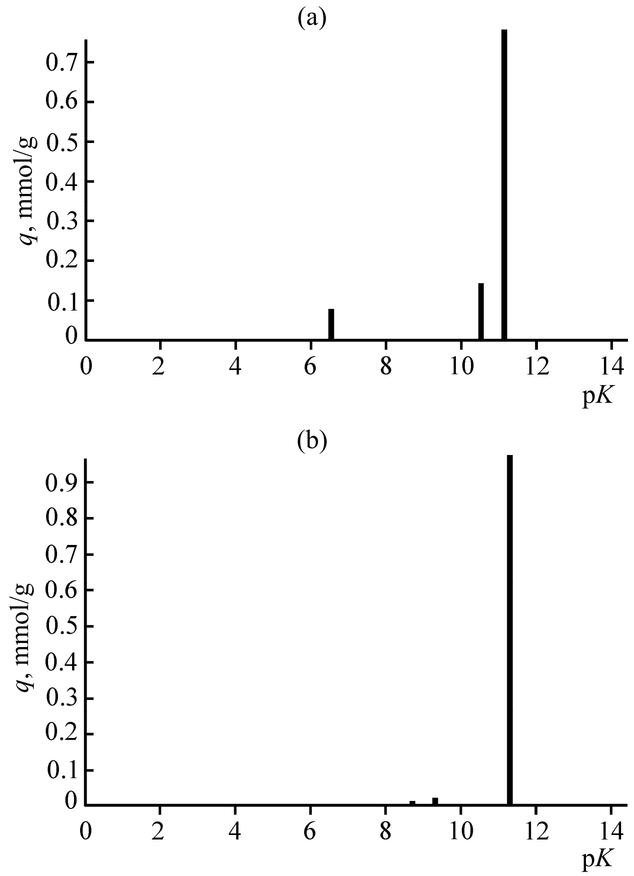


Fig. 3. p*K* spectra of FeO(OH) (a) and Fe_2O_3 (b).

Figure 2 shows p*K* spectra of various modifications of aluminum oxide. Following the 4p*K* model [9], the peaks in the spectra could be assigned to the following equilibriums:

$$\text{–Al–OH}_2^+ \rightleftarrows \text{–Al–OH} + H^+ \ (pK_1 \sim 4),$$

$$\text{–Al–OH} \rightleftarrows \text{–Al–O}^- + H^+ \ (pK_2 \sim 10\text{–}12),$$

$$\text{–Al–OH}_2^+Cl^- \rightleftarrows \text{–Al–OH} + H^+ + Cl^- \ (pK_3 \sim 7\text{–}8),$$

$$\text{–Al–OH} + Na^+ \rightleftarrows \text{–Al–O}^-Na^+ + H^+ \ (pK_4 \sim 8\text{–}10).$$

The pK_1 value significantly decreased in the γ-AlO(OH)–γ-Al_2O_3–α-Al_2O_3 series, being absent in the case of corundum. The equilibrium state corresponding to pK_2 was practically independent of alumina modification type.

Figure 3 displays p*K* spectra of iron hydroxide derivatives prepared via sol-gel route, FeO(OH) (Fig. 3a) and Fe_2O_3 (Fig. 3b). As seen from the plot, with increasing of annealing temperature water was eliminated to yield the surface acid-base sites, their behavior being described with the following equation: –Fe–OH ↔ –Fe–O^- + H^+ (pK_2 ~ 11). The acid-base sites corresponding to pK_1 equilibrium (the 4p*K* model) were not found at the surface.

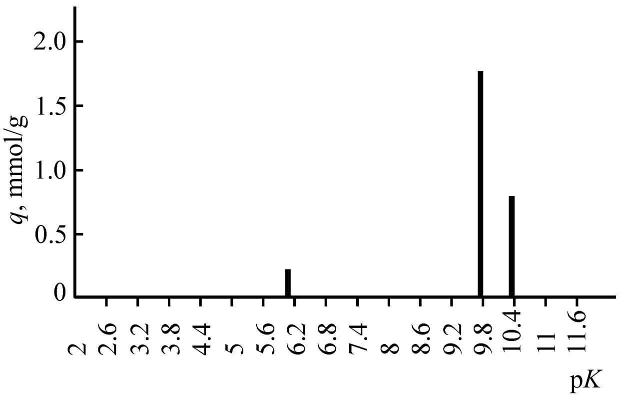


Fig. 4. p*K* spectrum of SiO_2 (aerosil).

Figure 4 shows p*K* spectrum of nanosized silicon oxide. Analysis of acid-base properties of SiO_2 usually involves the assumption that its surface charge changes due to dissociation of surface silanol groups [Eqs. (5) and (6)].

$$\text{–Si–OH}_2^+ \rightleftarrows \text{–Si–OH} + H^+ \ (pK_1 \sim 6), \quad (5)$$

$$\text{–Si–OH} \rightleftarrows \text{–Si–O}^- + H^+ \ (pK_2 \sim 10). \quad (6)$$

Ions of background electrolytes are known to form complexes with hydroxyl groups at silicon oxide surface. Likely, at least one layer of water molecules separate these weakly absorbed ions and the surface atoms of oxygen and silicon; this means that ion pairs or outer sphere complexes are formed [10]. Therefore, protolytic properties of silicon oxide additional reaction (7) should be considered (formation of outer sphere complexes with electrolyte cations).

$$\text{–Si–OH} + Na^+ \rightleftarrows \text{–Si–O}^-Na^+ + H^+ \ (pK_4 \sim 9\text{–}10). \quad (7)$$

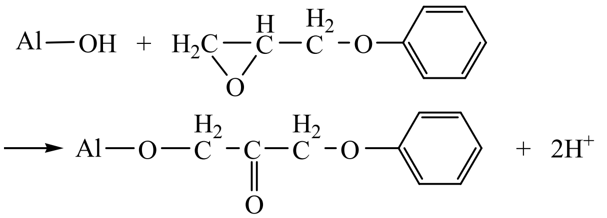
Differential scanning calorimetry DSC was applied to study the physico-chemical processes occurring upon addition of the powder oxides to phenyl glycidyl ether. The DSC traces of representative samples containing Al_2O_3 are shown in Fig. 5, and the corresponding interaction parameters are collected in the table.

From Fig. 5 it is to be seen that in the cases of γ-AlO(OH) and γ-Al_2O_3 the DSC curves contained exothermal peak assigned to chemical interaction of epoxy groups with the surface acid-base sites of the oxides, whereas such peak was absent in the case of α-Al_2O_3. Similarly to the latter case, DSC curves did not reveal any chemical interaction of the epoxide with the filler surface in the cases of iron and silicon oxides.

As the constants K_1 and K_2 reflect the strength of acid-base sites, the presence of pK_1 line at about 4 in the pK spectrum of γ-AlO(OH) and γ-Al_2O_3 confirmed the higher reactivity of those oxides as compared with other studied objects.

That was further confirmed by IR spectroscopy data. In particular, heating of mixture of phenyl glycidyl ether with γ-AlO(OH) (90°C, 1 h) led to weakening of the absorption bands assigned to vibrations of epoxy groups (750–950 cm^{-1}) (Fig. 6), thus confirming consumption of those groups in the course of phenyl glycidyl ether polymerization at the surface of alumina.

Appearance of the absorption band at 1650–1600 cm^{-1}, assigned to stretching of C=O conjugated with oxygen atom, suggested the following scheme of the epoxide ring opening (in the scheme, Al is aluminum atom at the filler surface).



Heating of the mixture of phenyl glycidyl ether with γ-Al_2O_3 led to significant weakening of the epoxy group absorption bands as well. Moreover, the bands assigned to vibrations of aliphatic C–O–C bonds appeared at 1150–1060 cm^{-1} (Fig. 7). Those spectral changes pointed at homopolymerization of phenyl glycidyl ether to yield polymeric ether, the alumina active sites acting as polymerization initiators.

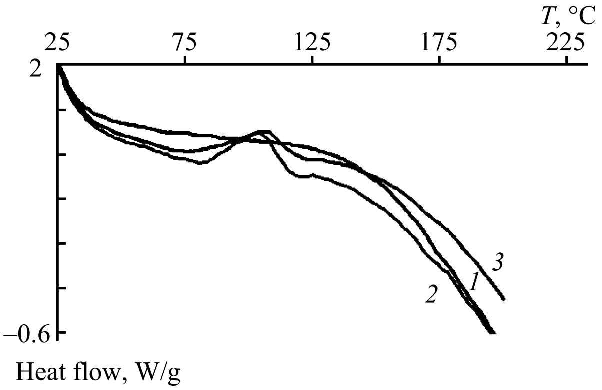
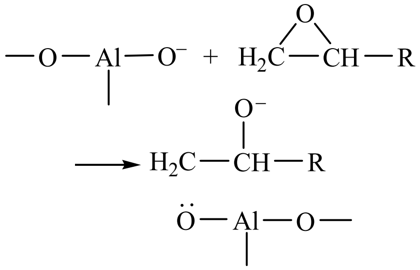


Fig. 5. DSC traces of the model mixtures based on phenyl glycidyl ether containing α-Al_2O_3 (*1*), γ-AlO(OH) (*2*), and γ-Al_2O_3 (*3*).



Besides the discussed interactions, IR spectra revealed appearance of the surface hydroxyl groups, similar to those present in γ-AlO(OH) (weak band at 1640–1630 cm^{-1}) (Fig. 7b). The hydroxyl groups appeared due to hydrolysis reaction [7].

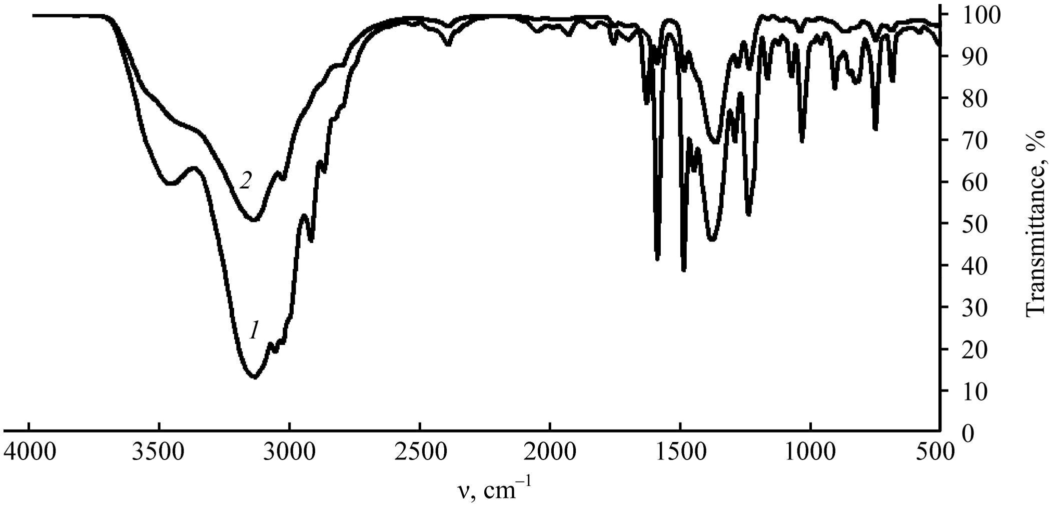


Fig. 6. IR spectrum of the phenyl glycidyl ether–γ-AlO(OH) mixture: before heating (*1*) and after annealing at 90°C during 1 h (*2*).

Thermal parameters and heat effect of interaction in the model mixtures of phenyl glycidyl ether with γ-AlO(OH) and γ-Al_2O_3

Oxide component	T_{start}, °C	T_{max}, °C	T_{end}, °C	Q, J/g
γ-AlO(OH)	80	105	125	8.6
γ-Al_2O_3	76	105	125	6.2

$$\text{–Al–O–Al–} + H_2O \rightleftarrows 2\text{–Al–OH}.$$

Heating of phenyl glycidyl ether mixed with other studied oxides did not lead to any changes of IR spectra.

To conclude, we demonstrated that of the studied oxides only γ-Al_2O_3 and γ-AlO(OH) contained the acid-base sites with behavior described by the $\text{–Al–OH}_2^+ \leftrightarrow \text{–Al–OH} + H^+$ equilibrium and pK_1 of about 4 (the 4pK model). Containing the reactive surface groups, those modifications acted as reactive fillers for epoxy polymers. In their mixtures with phenyl glycidyl ether, chemical interaction of epoxy rings with the surface hydroxyl groups of the oxide was observed as well as homopolymerization of phenyl glycidyl ether initiated by the active surface groups of the filler. Less reactive iron oxides, silicon oxide, and corundum did not participate in such interactions. The latter oxides could modify the polymer matrix properties due to formation of hydrogen bonds between epoxy groups and the surface acid-base sites of the oxides.

EXPERIMENTAL

Aluminum oxide was prepared by precipitation from saturated solution of aluminum nitrate (*analytical pure* grade) with aqueous ammonia (23 wt %, *chemical pure* grade); the precipitant was added till pH of 7.5 was reached. Various modifications of alumina were prepared by annealing of the synthesized aluminum hydroxide: at 300°C [γ-AlO(OH)], 650°C (γ-Al_2O_3), or 1200°C (α-Al_2O_3) during 1 h, after heating at 60 deg/h [11].

Derivatives of iron hydroxide were prepared via the sol-gel route from iron(III) chloride [12]. Silicon oxide was prepared by decomposition of silicon chloride (*chemical pure grade*) vapor with water vapor at 1000°C.

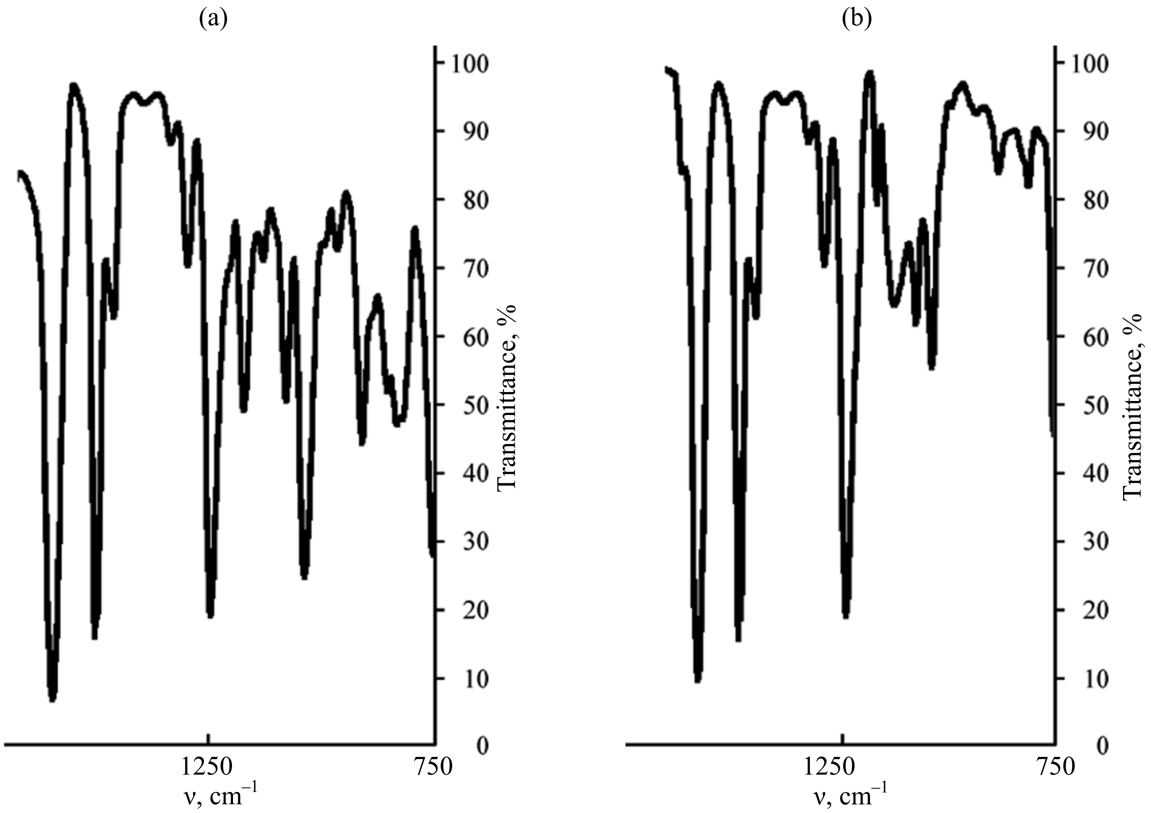


Fig. 7. Selected regions of IR spectra of the phenyl glycidyl ether–γ-Al_2O_3 mixture before heating (a) and after annealing at 90°C during 1 h (b).

The oxides acid-base properties were studied by p*K* spectroscopy. Specimens with suspended particles of 1–2 μm were used in the analysis. Prior to titration, the suspension pH was adjusted to 2–3, and the samples were incubated under those conditions during 1 day. In the course of titration, ionic strength of the suspension was maintained at 0.1 mol/L. Titration was performed at constant temperature (±0.2°C), under argon stream, in polypropylene flasks. As a rule, two parallel titrations were run to estimate the measurement accuracy.

DSC data were obtained using the Shimadzu DSC-60 differential scanning calorimeter at 2 deg/min heating rate in air.

IR spectra were recorded using the IRPrestige 21 spectrometer (KBr) after isothermal annealing at 90°C during 1 h.

The model epoxy-containing compound, phenyl glycidyl ether contained 26% of epoxy groups. It contained the only fragment capable of interaction with the filler surface, thus simplifying the procedure.

ACKNOWLEDGMENTS

This work was financially supported by basic research program of Ural Branch, Russian Academy of Science (projects nos. 12-33-004-ARKTIKA and 12-I-3-2005).

REFERENCES

1. Khozin, V.G., *Usilenie epoksidnyh polimerov* (Enhancing of Epoxy Polymers), Kazan: PIK “Dom Pechati,” 2004.
2. Baldan, A., *J. Mat. Sci*., 2004, vol. 39, no. 1, p. 1.
3. Morterra, C. and Magnacca, G., *Catal. Today*, 1996, vol. 27, p. 497.
4. Golikova, E.V., Ioganson, O.M., Fedorova, T.G., and Chernoberezhskii, Yu.M., *Poverkhnost. Fiz., Khim., Mekhan*.,1995, no. 9, p. 78.
5. *Khimiya privitykh poverkhnostnykh soedinenii* (Chemical Compounds of Grafted Surface), Lisichkin, G.V., Ed., Moscow: Fizmatlit, 2003.
6. Ryazanov, M.A. and Dudkin, B.N., *Colloid. J.,* 2004, vol. 66, no. 6, p. 726.
7. James, R.O. and Parks, G.A., *Surf. Colloid Sci*., 1982, vol. 12, no. 2, p. 119.
8. Ryazanov, M.A., *Izv. Komi Nauchn. Tsentra Ural. Otd. Ross. Akad. Nauk*, 2011, no. 2, p. 25.
9. Davis, J.A., James, R.O., and Leckie, J.O., *J. Colloid Interface Sci*., 1978, vol. 63, p. 480.
10. Vlasova, N.N., *Khimiya, fizika i Tehnologiya Poverkhnosti*, 2008, no. 14, p. 6.
11. Sitnikov, P.A., Belykh, A.G., Fedoseev, M.S., Vaseneva, I.N., and Kuchin, A.V., *Zh. Prikl. Khim*., 2008, vol. 81, no. 5, p. 789.
12. Krivoshapkin, P.V., Krivoshapkina, E.F., and Dudkin, B.N., *Glass Phys. Chem.,* 2012, vol. 38, no. 5, p. 449.