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Materials Science

New Polymer Composites on the Basis of Residual Polyethyleneterephtalate

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(Presented by Academy Member Tamaz Natriashvili)

New polymer composites on the basis of residual polyethyleneterephtalate and different fine dispersed mineral powders (andesite, bentonite, diatomite, liquid glass and quartz sand) were obtained and their mechanical (ultimate strength), thermal (temperature dependence of the softening) and water absorption properties were investigated. It was established that all properties of these materials were essentially improved, when the same fillers modified by tetraetoxysilane (TEOS) were used. Silane molecules create the "buffer" zones between filler and the homopolymer. This phenomenon is one of the reasons of increasing the strengthening of composites in comparison with composites containing unmodified fillers. The composites with modified diatomite display more high compatibility of the components than in case of the same composites with unmodified filler. The modified filler has stronger contact with polymer matrix (due to silane modifier) than unmodified diatomite. TEOS decreases fragility of composites increasing the compatibility of ingredients and decreasing the formation of the defects. *© 2021 Bull. Georg. Natl. Acad. Sci.*

Polyethyleneterephtalate, mineral fillers, polymer composite, mechanical and thermal properties

The polymer composites attract great attention of scientists and engineers. High monitoring of the exploitation properties in wide interval, high durability, stability to aggressive media, lightness, easy technology of obtaining and finally low cost are the fundamental characteristics of these materials. The noted factors lead to high competitiveness to such traditional materials as metals, ceramics, wood and skin. Currently the polymer (synthetic or natural) composites with different mineral fillers are widespread [1-7]. Thanks to these fillers many properties of the composites are improved: the durability and rigidity increases, the shrinkage during hardening process and water absorption decrease, thermal stability, fire proof and dielectric properties increase and finally the price of composites is reduced [3-5]. It is known that in general high molecular substances as "soft materials" reveal hydrophobic properties, high elasticity and durability in a wide range of filling and temperatures and consequently introduction of these materials to the polymer blends, in general, can increase compatibility of ingredients and respectively increase the mineral filler concentration in the composites [6, 7]. Since the price of mineral fillers is commonly very low than that of polymer (binder), the main investigation in the field of composite technology is directed to creation of high filled composite materials. If we foresee that the composites may be obtained on the basis of different natural or artificial wastes, the application of these materials will be connected with great economical effect.

The purpose of the present work is investigation of the effect of some minerals spread in Georgia modified by tetraethoxisilane on some physical properties of the composites. Besides, we tried enhancing the composite characteristics with the use of synergistic effect (enhancing composite characteristics at definite proportion of two or more filler types).

Experimental

The organic solvents were purified by drying and distillation. The purity of starting compounds was controlled by LKhM-8-MD gas liquid chromatography; phase SKTF-100 (10%, the NAW chromosorb, carrier gas He, 2m colomn). Chemical analysis of the obtained products was conducted on the spectrometer FTIR. Spectra were recorded on a Jasco FTIR-4200 device. Modify of the minerals with silicon-organic compounds tetraethoxisilane (TEOS) were used. The silanization reaction of minerals surface with TEOS were carried out by means of three-necked flask supplied with mechanical mixer, thermometer and dropping funnel. For obtaining of modified by 3 wt % mineral to a solution of 50 g finely ground mineral powder in 80 ml anhydrous toluene the toluene solution of 1.5 g (0.0072 mol) modifier in 5 ml toluene was added. The reaction mixture was heated at the boiling temperature of used solvent toluene. Than the solid reaction product was filtrated, the solvents (toluene and ethyl alcohol) were eliminated and the reaction product was dried up to constant mass in vacuum. Other product modified by 5 % modifier was produced via the same method.

The composites based on polyethyleneterephtalate (PETP) with different content of filler were obtained after careful mixing of components in mixer. The blend of ingredients was placed in the spatial (in accordance with ISO standards) forms and was heated till softening temperature. The concentration of fillers was changed in the range of 10–60 wt %.

The following characteristics of the obtained composites were defined: ultimate strength (on the stretching apparatus of type “Instron”), temperature dependence of the softening (by method Vica).

Results and Discussion

From mechanical parameters of the composites with bentonite the ultimate strengthening was investigated. The curves presented in Fig. 1 allow us to make a conception that this parameter increases up to definite maximum significances after which it decreases. The position of the maximums is defined with the content of the composite. The curve 1 corresponds to the composite containing the filler without modifier. The shape of this curve reflects well-known dependence for filled polymer composites. The mechanical strengthening of this composite with unmodified bentonite has the maximum at relatively low concentration of the filler (between 10 and 20 wt %), while this maximum for analogical composite with modified by TEOS (3 and 5 wt %) bentonite the noted maximum shares to higher concentrations of this filler (Fig. 1, curves 2 and 3). This result has practically important meaning – the higher the mineral filler concentration in the composite the lower its cost is. The curve 3 of this figure shows that the maximum in this case must be at filler concentrations higher than 40 wt %.

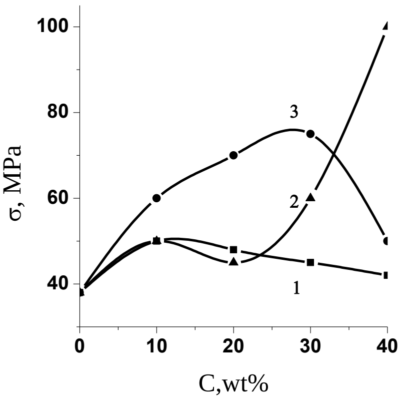

Fig. 1. Dependence of the ultimate strength of the composite PETP + bentonite on the concentration of the filler: unmodified bentonite (1); bentonite modified with 3 wt % of TEOS (2) and bentonite modified with 5 wt % TEOS

The curves of dependence of mechanical strengthening of the composites with modified and unmodified bentonite show that the modifier molecules displaced on the filler particle surface increase their activity (expressed with enhancing the composite material as a result of chemical reactions between active groups of ingredients) till definite concentrations of the filler, higher which the mechanical characteristics of composite decreases. One of the main reasons of this phenomenon is the formation of number of structural defects (mechanical cracks, empties) as a result of formation of the surfaces non reacted with organic part of the binder, amount of which increases with the increase of filler concentration. It is due to so called effect of high filling (or the Rebinder effect).

In the composites with modified fillers the characteristic maximums on the curve of dependence ultimate strengthening on the filler concentration modifier molecules enhance the interaction between heterogeneous phases from one side and absorb the mechanical stresses in composite body at hardening from other one. Therefore, the maximums on the curves for the composites with modified fillers are shared to higher concentrations of the filler. However, at further increase of filling in the composite the modifier phase increases, which is usually soft phase and plays the role of structural defects. The increase of this phase leads to softening or decrease of the composite mechanical strengthening.

The phenomena described above appear at investigation of the composite thermal mechanical properties.

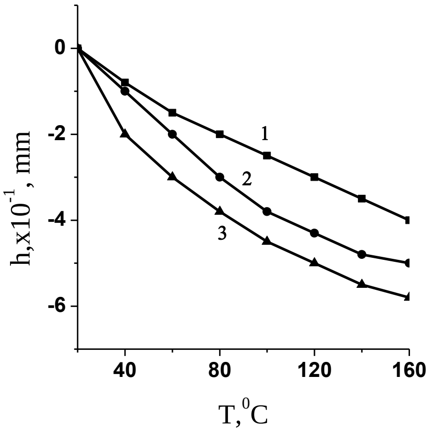

Fig. 2. Dependence of the softening on the temperature for composite with modified by 5 wt % (1) and 3 wt % TEOS (2), and for composite with unmodified filler (3); concentration of the bentonite in all samples 30 wt %.

From the curves presented in Fig. 2 it is seen that modified with TEOS bentonite as filler in the composite effects to definite extent on the thermal stability of the composite. Namely the softening of the composites containing modified by TEOS bentonite begins at relatively high temperatures than in case of ones containing unmodified filler. This result is in good agreement with ones obtained at investigation of the mechanical properties of corresponding materials.

The dependence of ultimate strength on the content of diatomite (modified and unmodified) presented in Fig. 3 shows that it has an extreme character. However, the positions of corresponding curves maximums essentially depend on the amount of modified agent TEOS. The general view of these dependences is in full conformity with the well-known dependence of σ – C [8]. Sharing of the maximum of the curve for composites containing 5 % of modified diatomite from the maximum for the analogous composites containing 3% modifier to some extent is due to the increase of the amount of the bonds between filler particles and macromolecules at the increase of the concentration of the filler.

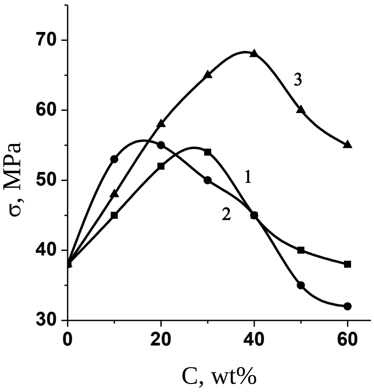

Fig. 3. Dependence of ultimate strength of the composites based on PETP with unmodified (1) and modified by 3 wt % (2) and 5 wt % (3) TEOS diatomite.

Investigation of the composite softening temperature was carried out by Vicat apparatus. Fig. 4 shows the temperature dependence of the indentor deepening to the mass of the sample for composites with fixed (20 wt %) concentration of unmodified and modified by TEOS.

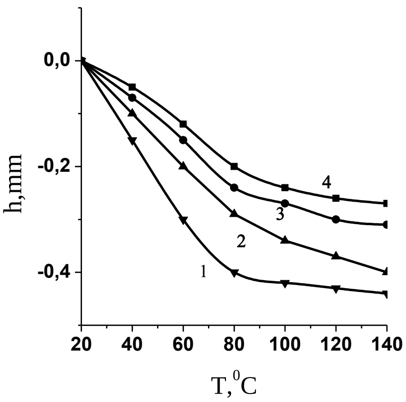

Fig. 4. Temperature dependence of the indentor deepening in the sample for composites containing 0 (1); 20 wt % (2); 20 wt % modified by 3% TEOS (3), 20 wt % modified by 5wt % TEOS (4) diatomite.

Based on the character of curves (see Fig. 4) it may be proposed that the composites containing diatomite modified by TEOS possesses thermo-stability higher than in case of analogous composites with unmodified filler. Probably the presence of increased interactions between macromolecules and filler particles due to modified agent leads to the increase of thermo-stability of composites with modified diatomite.

The obtained experimental results may be explained in terms of composite structure peculiarities.

Silane molecules displaced on the surface of diatomite and andesite particles lead to their activation of them and participate in chemical reactions between active groups of TEOS and homopolymer. Silane molecules create the "buffer" zones between filler and the homopolymer. This phenomenon may be one of the reasons of increasing strengthening of composites in comparison with the composites containing unmodified fillers. The composites with modified diatomite display higher compatibility of the components than in case of the same composites with unmodified filler. The modified filler has stronger contact with polymer matrix (due to silane modifier) than unmodified diatomite. Therefore, mechanical stresses formed in composites by stretching or compressing forces absorb effectively by relatively soft silane phases, i.e. the development of micro defects in carbon chain polymer matrix of composite districts and finishes in silane part of material the rigidity of which decreases.

The mechanical strengthening of the composite on the basis of different minerals and PETP increases at increasing of the filler concentration at once (till definite significations). Practically the dependence of the mechanical strengthening of the composite is coincided to well-known dependence with maximum of the polymer composite with inorganic (e.g. mineral) filler. When we introduce the high dispersed mineral modified with TEOS the changes appear at relatively low concentration of the modifier, the analogues composite containing modified by 3 wt % TEOS bentonite the maximum on the curve of dependence of ultimate strength on the filler concentration is shared to relatively high concentration of bentonite. This phenomenon is due to increasing the compatibility of ingredients in the composite. TEOS decreases fragility of composites and increases in the same time the compatibility of ingredients, decreases the formation of the defects, as empties. At high concentrations of bentonite so called effect of high filling appears, which is decreased under the influence of the modifier. The molecules of modifier at low concentrations (till formation of self phase) envelop the fillers particles and form the buffer zone between polymer matrix and filler. At more high concentrations of the modifier the formation of self phase of the modifier takes place.

The structural peculiarities of composites display also in thermo-mechanical properties of the materials. It is clear that softening of composites with modified by TEOS composites begins at relatively high temperatures. This phenomenon is in good correlation with corresponding composite mechanical strength. Of course the modified filler has stronger interactions (due to modifier) with polymer molecules, than unmodified filler.

Conclusions

Comparison of the ultimate strength and softening temperature for polymer composites based on PETP with minerals bentonite and diatomite nanofillers leads to conclusion that modifier agent tetraethoxysilane stipulates the formation of heterogeneous structures with higher compatibility of ingredients and consequently promote to enhancing of composites technical characteristics.

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მასალათმცოდნეობა

ახალი პოლიმერული კომპოზიტები ნარჩენი პოლიეთილენტერეფტალატის საფუძველზე

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მიღებულია პოლიმერული კომპოზიტები ნარჩენი პოლიეთილენტერეფტალატისა და სხვადასხვა წვრილდისპერსიული მინერალური ფხვნილების (ანდეზიტი, ბენტონიტი, დიატომიტი და კვარცის ქვიშა) საფუძველზე და შესწავლილია მათი მექანიკური და თერმული თვისებები. დადგენილია, რომ ამ მასალის ყველა თვისება არსებითად უმჯობესდება, როდესაც შემვსები მოდიფიცირებულია ტეტრაეტოქსისილანით (ტეოს). სილანის მოლეკულები ქმნიან „ბუფერულ" ზონებს შემავსებელსა და ჰომოპოლიმერს შორის. ეს ფენომენი არის კომპოზიტების გამლიერების გაზრდის ერთ-ერთი მიზეზი არამოდიფიცირებულ შემავსებლების შემცველ კომპოზიტებთან შედარებით. კომპოზიტები მოდიფიცირებული დიატომიტით აჩვენებენ კომპონენტების უფრო მაღალ თავსებადობას, ვიდრე არამოდიფიცირებული შემავსებლით შევსებული იგივე კომპოზიტები. მოდიფიცირებულ შემავსებელს უფრო ძლიერი კონტაქტი აქვს პოლიმერულ მატრიცასთან (სილანის მოდიფიკატორის გამო) ვიდრე არამოდიფიცირებულ დიატომიტს. ტეოსი ამცირებს კომპოზიტების სიმყიფეს და ერთდროულად ზრდის ინგრედიენტების თავსებადობას, ამცირებს დეფექტების წარმოქმნას.

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