

Improvement of Physical-Mechanical and Thermal Properties of Polymer Composites by Modification of Fillers

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(Presented by Academy Member Ramaz Gakhokidze)

Polymer composites are obtained on the basis of polyethylene production and household waste and various finely dispersed mineral powders (andesite and diatomite). Ultimate strength, softening temperature and water absorption of polyethylene-based polymer composites (type PE) with unmodified and/or modified by siliconorganic compound minerals have been studied. To improve the properties of the composite material, the method of modifying minerals with a low-molecular organo-silicon mixture - ethyl silicate was used. Comparison of experimental results obtained for investigated composites shows that the ones containing modified filler have better technical parameters than those with unmodified filler at corresponding loading. The modified filler has stronger contact with polymer matrix (due to silane modifier) than unmodified andesite. Siliconorganic compounds reduce the fragility of composites and at the same time, increase the compatibility of ingredients, decrease the formation of the defects, such as empties. Silane molecules create the "buffer" zones between filler and the homopolymer. This phenomenon is one of the reasons to increase the strengthening of composites compared to the composites containing unmodified fillers. It was experimentally shown that the composites containing binary fillers, diatomite and andesite, at a definite ratio possess optimal characteristics, the so-called synergistic effect. The obtained results are explained in terms of structural peculiarities of polymer composites. © 2023 Bull. Georg. Natl. Acad. Sci.

polymer composite, polyethylene, modified filler, ultimate strength, softening temperature, siliconorganic compounds, binary fillers

Recently, mineral fillers have attracted attention as active filling agents of polymer composites [1,2]. Thanks to these fillers, many properties of the composites are improved – the durability and rigidity are increased, shrinkage during hardening process and water absorption are decreased, thermal stability, fireproof and dielectric properties

are improved and finally, the price of composites becomes cheaper [3-5]. At the same time, it should be noted that the mineral fillers at high content lead to some impairment of different physical properties of composites. Therefore, the attention of the researchers is drawn to the substances, which would eliminate the mentioned leaks. It is known

that silicon organic substances (both low and high molecular) reveal hydrophobic properties, high elasticity and durability in wide range of fillings and temperatures [6,7].

The purpose of this work is to study the effect of modification with siliconorganic compounds of the mineral – andesite as main filler and same mineral with andesite (binary filler) on some physical properties of polyethylene based composites.

Materials and Methods

Mineral andesite was used as a filler. 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 column). FTIR spectra were recorded on a Jasco FTIR-4200 device.

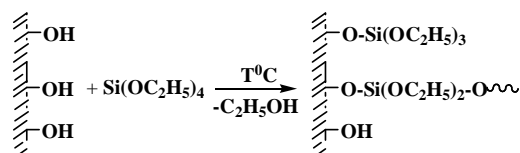
The silanization reaction of andesite surface with siliconorganic compounds was carried out by means of three-necked flask supplied with mechanical mixer, thermometer and dropping funnel. For obtaining of modified by 3 mass % diatomite, to a solution of 50 g grind finely andesite in 80 ml anhydrous toluene the toluene solution of 1.5 g (0.0072 mole) siliconorganic compounds in 5 ml toluene was added. The reaction mixture was heated at the boiling temperature of used solvent toluene. Then 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 products modified by 5% siliconorganic compounds was produced via the same method.

The following parameters were defined for obtained composites: ultimate strength (on the stretching apparatus of “Instron” type), softening temperature (Vicat method), density and water absorption (at saving of the corresponding standards).

Results and Discussion

High temperature condensation reaction between diatomite and silicoorganic compounds between

andesite on one side and the same modifier on the other side was carried out in toluene solution (~38%). The masses of silicoorganic compounds were 3 and 5% from the mass of filler. The reaction systems were heated at the solvent boiling temperature (383K) during 5-6 hours by stirring. The reaction proceeded according to the following scheme:



Scheme.

The direction of the reaction defined by FTIR spectra analysis has shown that after reaction between mineral surface hydroxyl, $-\text{OSi}(\text{OEt})_3$ and the $-\text{OSi}(\text{OEt})_2\text{O}-$ groups are formed on the surface of mineral particles.

In the FTIR spectra of modified andesite one can observe absorption bands characteristic of asymmetric valence oscillation for linear $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds at 1030 cm^{-1} . In the spectra, one can see absorption bands characteristic for valence oscillation of $\equiv\text{Si}-\text{O}-\text{C}\equiv$ bonds at 1150 cm^{-1} and for $\equiv\text{C}-\text{H}$ bonds at $2950-3000\text{ cm}^{-1}$. One can also see broadened absorption bands characteristic of unassociated hydroxyl groups.

On the basis of modified andesite and polyethylene the polymer composites with different content of filler were obtained after careful wet mixing of components in mixer. After this, the blends with hardening agent (polyethylene-polyamine) were placed to the cylindrical forms (in accordance with ISO standards) for hardening, at room temperature, during 24 h. Later, the hardened samples were exposed to temperature treatment at 393K during 4h.

The concentration of powder diatomite (average diameter up to 50 micron) was changed in the range of 10-60 mass %.

The curves in Fig.1 show that at increasing of filler concentration in the composites the density of

materials essentially depends both on filler content and the degree of concentration of modifying agent siliconorganic compounds. Naturally, the decrease of composite density at increasing of filler concentration is due to an increase in microvoids and their localization in the filler particles (Fig.1, curve 1). The composites with andesite modified by siliconorganic compounds contain smaller amount of empty areas as they are filled with modifying agent (Fig.1, curves 2 and 3).

The dependence of ultimate strength on the andesite content (modified and unmodified) illustrated in Fig. 2 shows that it has an extreme character. However, the position of corresponding curves maxima essentially depends on the amount of modified agent siliconorganic compounds. The general view of these dependences is in full conformity with well-known dependence of $\sigma - C$ [8]. The sharing of the maximum of curve for composites containing 5% of modified andesite from the maximum for the analogous composites containing 3% modifier to some extent is due to increasing of the amount of the bonds between filler particles and macromolecules at increasing of the concentration of the filler.

The investigation of composites softening temperature was carried out using the Vicat apparatus method. Figure 3 shows the temperature dependence of the indenter deepening to the mass of the sample for composites with fixed (20 mass %)

concentration of unmodified and modified by siliconorganic compounds.

Based on the character of curves in Fig. 3 it may be proposed that the composites containing diatomite modified with siliconorganic compounds possess higher thermostability than in case of analogous composites with unmodified filler. Probably the presence of increased interactions between macromolecules and filler particles due to modifying agent leads to increasing the thermostability of composites with modified andesite.

The effect of silane modifier on the investigated polymer composites is also revealed in the water absorption.

Such approach to microstructure of composites with an optimal ratio of the composite ingredients allows supposing that these composites would possess high mechanical properties, thermostability and low water absorption. Moreover, the composites with the same concentrations of the fillers modified by siliconorganic compounds possess all the above properties better than the composites with unmodified by siliconorganic compounds binary fillers, which may be proposed earlier. Indeed, the curves in Fig. 4 show that the maximum ultimate strength, thermostability and simultaneously hydrophobicity correspond to composites with the same ratio of fillers which corresponds to maximum density.

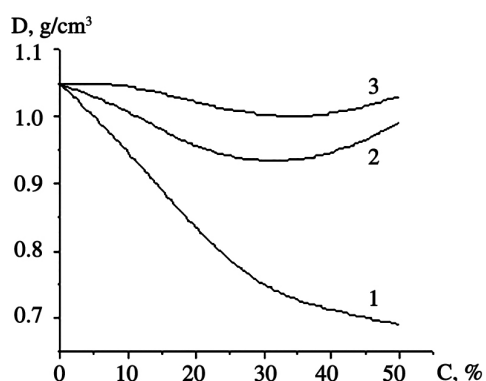


Fig. 1. Dependence of the density of the composites based on polyethylene (PE) on the concentration of unmodified (1), modified by 3% (2) and 5 mass % (3) siliconorganic compounds andesite.

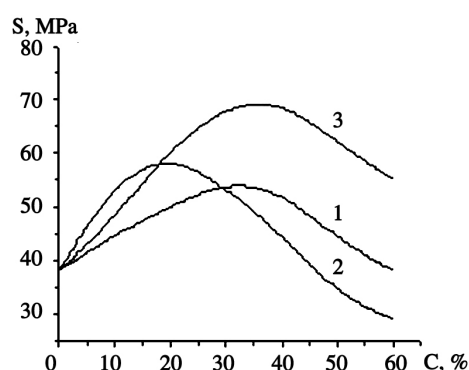


Fig. 2. Dependence of ultimate strength of the composites based on PE with unmodified (1) and modified by 3 (2) and 5 mass % (3) siliconorganic compounds andesite.

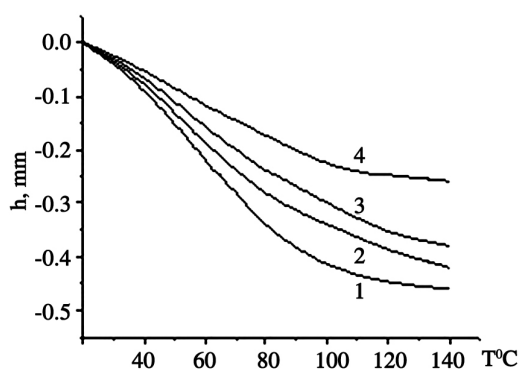


Fig. 3. Temperature dependence of the indenter deepening in the sample for composites containing (1), 20 mass % (2), 20 mass % modified by siliconorganic compounds 3% (3), 20 mass % modified by 5% siliconorganic compounds (4) andesite.

The obtained experimental results may be explained in terms of peculiarities of the composite structure. Silane molecules displaced on the surface of diatomite and andesite particles lead to their activation and participate in chemical reactions between active groups of siliconorganic compounds (hydroxyl) and homopolymer (epoxy group). Silane molecules create “buffer” zones between filler and the homopolymer. This phenomenon may be one of the reasons of increasing the strengthening of composites in comparison with composites containing unmodified fillers. The composites with modified diatomite display higher compatibility of the components than the same composites with unmodified filler. The modified filler has a stronger contact with polymer matrix (thanks to the silane modifier) than unmodified diatomite. Therefore, mechanical stresses formed in composites by stretching or compressive forces are effectively relatively absorbed by soft silane phases, i.e. the development of microdefects in carbon-chain polymer matrix of composite districts and finishes in silane part of the material, the rigidity of which decreases.

The structural peculiarities of composites are also displayed in thermomechanical properties of the materials. It is clear that the softening of compo-

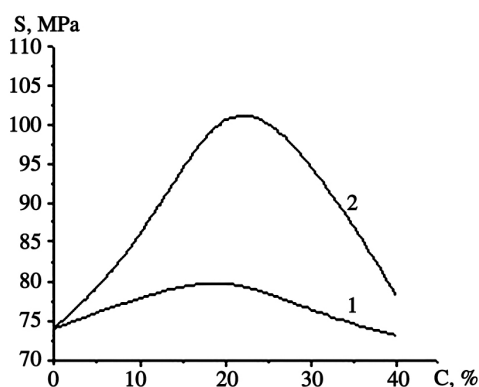


Fig. 4. Dependence of the ultimate strength on the concentration of diatomite in binary fillers with andesite. (1) - unmodified fillers and modified by 5% siliconorganic compounds (2) ones for composites based on polyethylene. Full concentration of binary filler in composites 50 mass.

sites with modified siliconorganic compounds composites begins at relatively high temperatures. This phenomenon is in good correlation with corresponding composite mechanical strength. Of course, the modified filler has a stronger interaction (thanks to the modifier) with polymer molecules than unmodified filler.

The amplified competition between the filler particles and macromolecules by siliconorganic compounds is also well reflected in the water absorption characteristics. In general, loosening of microstructure because of microvoids is due to the increase in filler content. The formation of such defects in the microstructure of composite promotes water absorption processes. Water absorption of composites with modified diatomite is to some extent lower than with unmodified filler. The decrease in water absorption of composites containing silane compound is the result of their hydrophobic properties.

Composites with binary fillers possess so-called synergistic effect - a non-additive increase in technical characteristics of composites containing the fillers at a definite ratio, which is due to the creation of the dense distribution of ingredients in composites.

Conclusion

Comparison of the density, ultimate strength, softening temperature and water absorption of polymer composites based on polyethylene (PE type) which is unmodified and/or modified by siliconorganic compounds mineral fillers leads to the conclusion that modifying agent stipulates the formation of heterogeneous structures with higher

compatibility of ingredients and consequently to enhancing of the above technical characteristics.

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ორგანული ქიმია

პოლიმერული კომპოზიტების ფიზიკურ-მექანიკური და თერმული თვისებების გაუმჯობესება შემავსებელთა მოდიფიკაციის გზით

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(წარმოდგენილია აკადემიის წევრის რ. გახვიძის მიერ)

მიღებულია პოლიმერული კომპოზიტები პოლიეთილენის საწარმო და საყოფაცხოვრებო ნარჩენებისა და სხვადასხვა წვრილდისპერსიული მინერალური ფხვნილების (ანდეზიტისა და დიატომიტის) საფუძველზე. შესწავლილია მიღებული კომპოზიტების ფიზიკურ-მექანიკური და თერმული თვისებები. კომპოზიციური მასალის თვისებათა გაუმჯობესების მიზნით გამოყენებულია მინერალების მოდიფიცირების მეთოდი დაბალმოლეკულური ორგანული სილიკონური ნარევით - ეთილსილიკატით. დადგენილია, რომ კომპოზიციური მასალის ყველა თვისება არსებითად უმჯობესდება, როდესაც შემავსებლები მოდიფიცირებულია სილიკონ-ორგანული ნარევის-ეთილსილიკატის საშუალებით. კომპოზიტები მოდიფიცირებული ანდეზიტით აჩვენებს კომპონენტების უფრო მაღალ თავსებადობას, ვიდრე არამოდიფიცირებული ანდეზიტით შევსებული იგივე კომპოზიტები. ეს ფაქტორი განპირობებულია ე.წ. „ბუფერული“ ზონებით, რომლებსაც სილანის მოლეკულები წარმოქმნის შემავსებლის მარცვლებსა და ჰომოპოლიმერის მაკრომოლეკულებს შორის. ამის გამო მოდიფიცირებულ შემავსებელს

უფრო ძლიერი კონტაქტი აქვს პოლიმერულ მატრიცასთან, ვიდრე არამოდიფიცირებულ შემავსებელს. ძლიერდება თავსებადობა შემავსებლის მარცვლებსა და პოლიმერის მაკრომოლეკულებს შორის, რაც განაპირობებს კომპოზიციური მასალის ფიზიკურ-მექანიკური და თერმული თვისებების ზრდას. ეთილსილიკატი ამლიერებს რა ინგრედიენტების თავსებადობას, ამცირებს კომპოზიტების სიმყიფეს და მასალაში დეფექტების წარმოქმნას, რის გამოც მცირდება კომპოზიტების წყალშთანთქმა. მიღებულია აგრეთვე, პოლიმერული კომპოზიტები ბინალური (ორმაგი) შემავსებლებით, კრძოდი, ანდეზიტი/დიატომიტი. შემავსებელთა გარკვეული თანაფარდობისას ადგილი აქვს „სინერგიულ ეფექტს“, რომელიც კომპოზიციური მასალის ფიზიკურ-მექანიკური და თერმული თვისებების გაზრდის ერთ-ერთი მიზეზია. კომპოზიტები მოდიფიცირებული ბინალური (ორმაგი) შემავსებლებით (ანდეზიტი/დიატომიტი), აჩვენებს კომპონენტების უფრო მაღალ თავსებადობას, ვიდრე არამოდიფიცირებული შემავსებლით შევსებული იგივე კომპოზიტები და, შესაბამისად, უფრო მეტად გაუმჯობესებულ საექსპლუატაციო თვისებებს.

REFERENCES

1. Katz H.S., Milevski J.V. (1987) Handbook of fillers for plastics, RAPRA, NY, USA.
2. Mareri P., Bastrole S., Broda N., Crespi A. (1998) Mechanical behaviour of polypropylene composites containing fine mineral filler: Effect of filler surface treatment. *Composites Science and Technology*, **58**(5): 747-755.
3. Tolonen H., Sjolind S. (1996) Effect of mineral fillers on properties of composite matrix material. *Mechanics of Composite Materials*, **31**(4): 317-322.
4. Rothon S. (2003) Particulate filled polymer composites, RAPRA, NY, USA.
5. Lou J., Harinath V. (2004) Effects of mineral fillers on polystyrene melt processing. *Journal of Materials Processing Technology*, **152**(2): 185-193.
6. Khananashvili L.M., Mukbaniani O.V., Zaikov G.E. (2006) Monograph, new concepts in polymer science, «Elementorganic monomers: technology, properties, applications». Netherlands, VSP/, Utrecht.
7. Aneli J.N., Khananashvili L.M., Zaikov G.E. (1998) Structuring and conductivity of polymer composites, 323-326. *Nova Sci. Publishers*, New-York. USA.
8. Zelenev Y.V., Bartenev G.M. (1978) Fizika polimerov. Visshaia shkola M. (in Russian).

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