

УДК 678.028

V. N. Noskova, PhD student (VSETU);
G. V. Popov, D. Sc. (Engineering), professor (VSETU);
T. I. Igumenova, PhD (Engineering), assistant professor (VSETU);
N. L. Kleymenova, PhD (Engineering), assistant professor (VSETU);
K. V. Vishnevskiy, PhD (Engineering), assistant lecturer (BSTU)

USING METHOD DIFFRACTOMETER TO IDENTIFICATION MICROQUANTITIES OF NANOMATERIALS IN POLYMERS

The possibility of identification of trace amounts of nanomaterials in polymers by diffractometry was investigated. As elastomeric matrices used samples based on styrene-butadiene (SBR), natural isoprene (NC), ethylene propylene diene (EPDM) rubbers. Processing of the results of diffractometric analysis with the release of the main components, which affects the reflectivity of the surface of the composites was carried out. Containing of carbon fullerenes C_{50} – C_{92} fraction ranged from 0.005 to 1.0 phr. The dependence of the change in the agglomerate size with a maximum intensity of reflection was obtained.

Introduction. Problem of identification of components in complex mixtures of different purpose acquires special applicability in connection with development of nanomaterials production branch and development of new technologies and their use [1]. As a rule the modifiers of nanosized range from 1 to 100 nm are used in microdosage (less than 0.1%) and their presence can be only detected due to sudden change of physical and mechanic or chemical features of products with use of destructive analysis methods. The use of generally accepted methodic approaches used for polymer analysis does not allow estimating neither influence nor presence of nanoparticles in polymer compounds; that is why development of special research methods for high-molecular compositions is necessary.

We should mention that traditionally used methods in material science do not allow to evaluate specific features of structure, morphology and sizes, self-organizing supermolecular structures in full scope due to constructive or methodical limitations of instrument base. Diffraction analysis is one of the methods which is rarely used for polymer system properties analysis. It is first of all connected with difficulties of interpretation of the achieved results due to complex structure of high-molecular compositions and a range of factors, directly or indirectly influencing the result of the tests.

So, the identification of the content of polymer material is a complex multilevel task which needs long time for tests and is based on deep knowledge of the principles of material science, needs use of modern equipment and software.

Main part. As research objects were chosen: styrene-butadiene-rubber (SBR), isoprene rubber (IR), ethylene-propylene-diene rubber (EPDR) and mixture of carbonic C_{50} – C_{92} particle buckminsterfullerenes with the following mixture ratio: C_{50} – C_{58} (14.69%), C_{60} (63.12%), C_{62} – C_{68} (5.88%), C_{70} (13.25%), C_{72} – C_{92} (3.06%) as modifying additive.

Polymer and modifier mixtures in different concentrations were prepared in laboratory conditions by mixture in feed mill at temperature of 50–55°C, trace concentrations of buckminsterfullerenes were included into polymers by mixture of the necessary amount and films of the corresponding rubber after drying of toluene solutions of the mixture of buckminsterfullerenes on their surface. Evaluation of effect of variation of trace concentration of carbonic C_{50} – C_{92} particle buckminsterfullerenes on surface reflectivity of rubbers within the interval from 0 to 0.1 weight parts of buckminsterfullerenes mixture to 100 weight parts of the corresponding rubber.

X-ray diffraction analysis of polymer and buckminsterfullerenes compounds was performed on general-purpose diffractometer DRON-2, designated for different X-ray diffraction analyses of ordered structure of different materials.

Application of special peripheral equipment allows performing researches with wide coverage of reflection angular range; in range of temperatures from +20 to +2000°C and from +20 to –180°C. The working principle of diffractometer is based on creating of low-energy X-ray in BSV-2tube and beam focusing with the system of slots on vertical gripe with the sample. At interreacting of x-radiation with crystal lattice or textural features of substance the beams diffract and concentrate in scintillation detector. With photoconverters and reinforces the X-ray quants convert into current flow signals recorded by electronic digital computer and registered by a secondary instrument.

Calculations were made according to the famous Wolf-Bragg law, the dependencies of agglomerate size “rubber-buckminsterfullerenes” of Buckminsterfullerenes compound concentration were received. The excerpting was made for five tests for each sample and it was organized for convenience of calculations. The received experimental data is shown in the table.

**The dependence of the size of agglomerates of polymer-fullerene
on the concentration of the fullerenes mixture**

Test number	Concentration of the mixture of fullerenes, wt. PM			
	0	0.005	0.50	1.00
Butadiene-styrene rubber, the size of the agglomerate, nm				
1	173.21	173.36	173.65	208.32
2	173.28	173.43	173.80	249.85
3	173.28	173.50	185.99	249.91
4	173.36	173.58	202.99	270.44
5	173.36	203.36	224.96	271.02
Scope	0.15	30.00	51.30	62.70
Average	173.30	179.45	192.28	249.91
Natural polyisoprene, the size of the agglomerate, nm				
1	173.58	216.51	219.78	226.50
2	156.77	208.76	222.55	237.65
3	156.77	215.55	232.23	244.31
4	186.60	218.58	237.30	267.66
5	198.47	239.27	249.27	270.44
Scope	24.90	22.80	29.49	43.90
Average	174.44	221.53	232.23	249.31
Ethylene-propylene rubber, the size of the agglomerate, nm				
1	173.28	220.95	226.72	198.39
2	173.36	229.49	236.35	242.41
3	173.50	243.28	242.61	250.30
4	183.94	243.32	243.21	252.71
5	191.61	232.55	264.23	277.15
Scope	18.30	11.60	37.50	78.80
Average	179.14	233.92	242.63	244.19

One can see that by increasing of concentration of buckminsterfullerenes compound average sizes of new structures (agglomerates) increase proportionally too, at that deviation of the data is also increasing at replicate tests. This phenomenon is connected with the fact that certain buckminsterfullerenes in the compound solubilize expansion ends (segments) of rubber macromolecules, at that tie point of different functionality are made; at that functionality is the amount of certain macromolecules interacting by one segment with one molecule of buckminsterfullerene. At that we can't exclude the moment when one rubber macromolecule interreacts with buckminsterfullerene by more than one segment, establishing complicated joint and changing its structure. Formation of structures with joints of complex functionality begins at presence of buckminsterfullerenes in minimal concentration, at increasing of concentration the process is faster, the polymer properties change and the increase of data deviation implies intensity of physical processes.

At general analysis of the received digital data, where the presence of agglomerates of bigger size at any concentration of buckminsterfullerenes was detected. The intensity of such reflexes is not big (lower than 90 units) and manual data processing was difficult due to lengthy excerpts.

Further processing of digital results of diffractometric sample test of styrene-butadiene-rubber, isoprene rubber, ethylene-propylene-diene rubber was done with mathematical method of principal components [2], which is a sort of multicorrelation analysis. As principal determining component for data selection of regression analysis interval of interference intensity (90–100 units) at reflection on small angles (20°) was chosen. At application of the method of principal components we presumed that several measured variables have strong correlation. This means that either they shape each other or the correlation between them is stipulated by a tertium quid, which can't be directly measured. For calculations principal components were selected and the level of correlation between the factors and the variables was determined. If the correlation factor made 0.7, then the group was selected; if the target value wasn't achieved, data enumerating taking into account other factors till achievement of the necessary level of correlation was done. The aim of the performed factor analysis [1] was to extract concealed information of internal and external factors from masses of experimental data, which determine the system behavior, in this case polymer-buckminsterfullerenes structure formation.

The main methodology of the chosen method of factor analysis is to cancel the amount of va-

riables for analysis at the first stage (data reduction) and to determine the correlation structure between the variables. The factors are successively selected one by one as independent from each other. The selection of another factor decreases the data variability, which means the level of extracted dispersion is constantly decreasing [3].

In the result one should mention that polyisoprene is characterized by partial crystallite rearrangement at interreaction with buckminsterfullerenes at first, and then formation of functional joints. The same phenomenon is observed for ethylene-propylene-diene rubber, characterized by micro block structure "ethylene-propylene". In general for all types of rubbers the phenomenon has generic character and solubilization energy makes approximately one value in the amount of 2.6–3.2 kJ/mole.

Conclusion. A range of dependencies of the change of sizes of agglomerates of polymers with buckminsterfullerenes in reflection intensity was achieved, which allows detecting presence of microquantities of modified nanomaterials and esti-

mate their concentration by nonobtrusive method for sample. The method uses very small quantities of material for analysis and is nonobtrusive.

Application of mathematical method of factor analysis (principal components) for diffraction analysis data processing allows selecting principal interreactions in the system and make statistically accurate analysis of formation of new structures of polymer at its physical and chemical modification by carbonic nanomaterials in percolation concentration.

References

1. Игуменова Т. И., Чичварин А. В. Дискриминантный анализ спектральных характеристик пересаженных каучуков, модифицированных смесью фуллеренов группы C_{50} – C_{92} // Вестник ВГУ. 2012. № 2: Химия. Биология. Фармация. С. 12–19.
2. Иберла К. Факторный анализ. М.: Статистика, 1980. 398 с.
3. Лоули Д., Максвелл А. Факторный анализ как статистический метод. М.: Мир, 1967. 144 с.

Received 26.02.2014