Computer modelling of the molecular interactions and local dynamics of butadiene-acrylonitrile rubbers of different microstructures

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Currently the range of products and materials involving butadiene-acrylonitrile rubbers (BNR) in their manufacture numbers more than 100,000. The consumption of BNR in industry is around 10% of the total volume of consumption of all synthetic rubbers. This is due to a combination of oil and petrol resistance and the elasticity of BNR for its relatively low cost (ref. 1).

Recently paraffinate rubbers such as BNKS have tended to be used in Russia instead of the sulphonate rubbers of the type SKN (nitrile rubber); and there has been an expansion in the range and higher consumption of non-Russian types of butadiene-nitrile rubber (ref. 2).

Despite the similar chemical nature of SKN and BKNS rubbers there are some differences between them, resulting in the need to adjust the formulation and processing parameters for the production of rubber compounds. It is important to get an accurate idea of the microstructural characteristics of BNKS rubbers as compared with SKN in order to carry out theoretical and experimental studies.

In a comparative analysis of the microstructure of the butadiene-nitrile rubbers using IR spectroscopy it was found that in all the rubbers the greater part of the butadiene units consists of 1,4 units (about 87 – 91%), most of which are trans-1,4 (74 – 80% of the total number of butadiene units). The relative percentage of trans-1,4 units of butadiene increases somewhat with increase in the content of nitrile groups.

Units in polybutadienes having different configurations are known to have different mobility. This must obviously show up in copolymers and hence must also have an effect on the mobility of the acrylonitrile units.

We studied the influence of the microstructure of the rubbers on the energy of molecular interaction by means of computer modelling, in particular using the methods of molecular mechanics (ref. 3) and molecular dynamics (ref. 4).

An analysis was carried out of the structure of associates by calculating the geometry of the molecules forming the associate at a minimum of potential energy. The number of molecules in the associate varied from 20 to 32. We studied associates consisting of molecules of: 1) nitrile of propionic acid (propionitrile), 2) 2-butene, 3) 1,3-butadiene, 4) propionitrile and 2-butene (1:1 ratio) and 5) propionitrile and 1,3-butadiene (1:1 ratio).

It was established that the associates consisting of propionitrile molecules have the lowest total energy (Figure 1).

![Figure 1. Total potential energy of associates of 2-butene (curve 1), 1,3-butadiene and propionitrile (curve 2), 1,3-butadiene (curve 3), 2-butene and propionitrile (curve 4) and propionitrile (curve 5) vs. number of molecules in the associate.](image)
In this case the energy of molecular interaction for a single molecule is the greatest in comparison with other associates examined, which is due to the presence of polar nitrile groups.

It was shown that the greatest contribution to the total potential energy of associates consisting of molecules of 2-butene and 1,3-butadiene is made by the interactions between atoms more distant from each other along the chain than the atoms in the 1,4 positions ("non-1,4-van der Waals interactions"), and in the case of an associate consisting of propionitrile molecules by dipole-dipole interactions. Dipole-dipole interactions also show up in associates consisting of molecules of 2-butene. However, in this latter case the contribution of this interaction to the total energy has a positive sign, which indicates the presence of forces of repulsion between the molecules. The energy values of "non-1,4-van der Waals" interaction and "1,4-van der Waals" interaction of associates consisting of molecules of different types occupy an intermediate position compared to the energies of associates consisting of molecules of the same type. Associates consisting of different types of molecules are characterised by relatively small dipole-dipole interactions.

It was of interest to assess the influence of the length and microstructure of the molecules on the molecular interactions of chains of copolymers of butadiene and acrylonitrile. We studied model chains of butadiene-acrylonitrile (BN) copolymers of different lengths with 1,4-cis and 1,4-trans units of butadiene. The results of the calculations in the form of relationships between the total energy of the associates and the number of molecules in the associate are shown in Figure 2.

Calculation of the equilibrium conformations of associates showed that associates with 1,4-trans units of butadiene have the lowest total energy, owing to the more stretched molecular conformation and the resulting denser packing of the molecules in the associate. With increase in the number of units from three to six the total energy of the associates also decreases.

In order to assess the influence of the microstructure of the chains of butadiene-nitrile copolymers on the molecular mobility of the chain by the method of molecular dynamics, using a specialised ChemD program pack, we calculated the distributions of the conformations of polymer molecules consisting of different numbers of butadiene and acrylonitrile units (Figure 3). In the course of the calculation we determined the following structural parameters of the associate: the average distance between the terminal carbon atoms in the chain, the average distance between the nitrile groups of the polymer chains — in the temperature range from 1 to 400 K. In the low-temperature region (of the order of 1 – 3 K) for a chain with 1,4-cis units of butadiene there is a sharp decrease in the average distance between the terminal atoms of carbon, which points to a transition of the molecule to a globular conformation. On the other hand, the average distance between the terminal carbon atoms of the chain with 1,4-trans units of butadiene remains practically unchanged up to 300 K. At high temperatures, when forces of intra- and intermolecular interaction are compensated by thermal motion, the molecules take on the form of a statistical globule and the two curves draw nearer. A similar picture is observed with the temperature dependence of the average distance between nitrile groups.

The difference in the molecular mobility of copolymers having different configurations of the butadiene units is also confirmed by the calculated standard deviations of the distances between the end groups of the chain (Figure 4). As the temperature is raised there is an increase in the fluctuations of the distance between the ends of the molecules because of an acceleration in thermal motion, and a chain with 1,4-trans butadiene units is characterised by the greatest fluctuations as a result of the retarded transition to globular form as compared with a chain consisting of 1,4-cis units.
Thus, the molecules of butadiene-acrylonitrile rubbers containing 1,4-cis and 1,4-trans units of butadiene differ in their mobility and level of molecular interaction. The energy of molecular interaction between nitrile groups in copolymers containing 1,4-trans butadiene units is higher as a result of the denser packing and lower local mobility.

REFERENCES


(Received 18/07/2001)