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N.B. Arzumanova
(Institute of Polymer Materials of Azerbaijan National Academy of Sciences, Sumgait)

RHEOLOGICAL PARTICULARITIES OF NANOCOMPOSITES BASED ON RANDOM POLYPROPYLENE AND CLINOPTILOLITE

At present, polymer composites based on a thermoplastic matrix find a wide range of applications in various fields of engineering and technology. The main bulk of thermoplastics is processed through the melt and the most common industrial methods of processing them into products are: free casting, injection moulding, extrusion, press moulding, etc. When forming polymer materials, flow processes under shear deformation are of primary importance. Therefore, the rheological properties of filled polymer systems have always attracted the attention of researchers, since they were practically important when choosing the conditions for their processing into products. With the advent of nanocomposites based on polymer matrices, interest in such systems has multiplied. Moreover, if a structure formed by filler particles is formed in the melt, the rheological properties are largely determined by such a structure. The rheological properties of the polymer medium also play a paramount role and affect the rheological behavior of filled systems in different ways. [1]. Rheological studies are the key of successfully giving fundamental insight into the flow behavior, helping to determine the optimum processing conditions, in the cases of polymer processing such as extrusion and injection molding [2].

In this regard, the aim of this work was, using the example of natural mineral filler and a polyolefin, to show the predominant, from a rheological point of view, features of nanocomposites obtained on their basis. The South Korean Industrial grade RP2400 random polypropylene was selected as a polymer matrix. Clinoptilolite of the Aydag deposit of Azerbaijan was used as a mineral filler, the typical oxide formula of which is $(Na_2K_2)OAl_2O_3{\cdot}10SiO_2{\cdot}8H_2O$. X-ray phase analysis of clinoptilolite showed that its composition mainly includes: clinoptilolite – 70-75%, kaolinite – 12%, potassium feldspar – 3-5% and other impurities. Clinoptilolite particle size was 10-110 nm.

Rheological measurements were carried out in a CEAST MF-50 capillary rheometer (*İnstron, İtaly*) at four temperatures (from 190 to 250°C) and five loads (from 3.8 to 21.6 kg). The rheometer was equipped with a nozzle having a ratio of capillary length to diameter equal to 24.

Rheological studies carried out in a wide range of temperatures and shear stresses allow a deeper look at the processes occurring in the polymer melt. This is especially important when it comes to filled polymer composites. The study of this problem becomes even more relevant when considering polymer composites using nanosized mineral fillers. According to some researches, the improvement of the properties of composites is determined by the fact that nano-particles interact with each other and with the matrix differently than large particles. The distance at which this interaction takes place is commensurate with the size of the particles themselves [3].

It was found that the introduction of clinoptilolite leads to a decrease in the viscosity of nanocomposites based on them. In order to verify this, the flow curves of the initial random polypropylene and its nano-filled compositions with clinoptilolite, the dependence of the melt viscosity on temperature, shear rate and filler concentration were studied. Figure 1 shows the rheological flow curves of the original thermoplastics and the filled composite based on it. By analyzing the flow curves in Fig. 1(a), it can be established that they are S-shaped in a wide range of shear stresses. According to these data, the presence of two branches close to the region of the Newtonian flow is clearly noted on the flow curves. The lower branch characterizes the region of greatest Newtonian viscosity, and the upper branch - the smallest Newtonian viscosity. The middle section is called the structural branch and characterizes the non-Newtonian region of the polymer melt flow. With a change in shear stress occurs a change in the viscosity of the melt on it. If in the region close to the highest Newtonian viscosity (Fig. 1, a), an increase in temperature from 190 to 250°C at lgτ=3.68 leads to a sharp increase in the shear rate, then in the region of the lowest Newtonian viscosity, an increase in temperature at lgτ=4.52 is accompanied by a change in shear rate to a relatively lesser extent. A similar character of the change in the shear rate from temperature was also

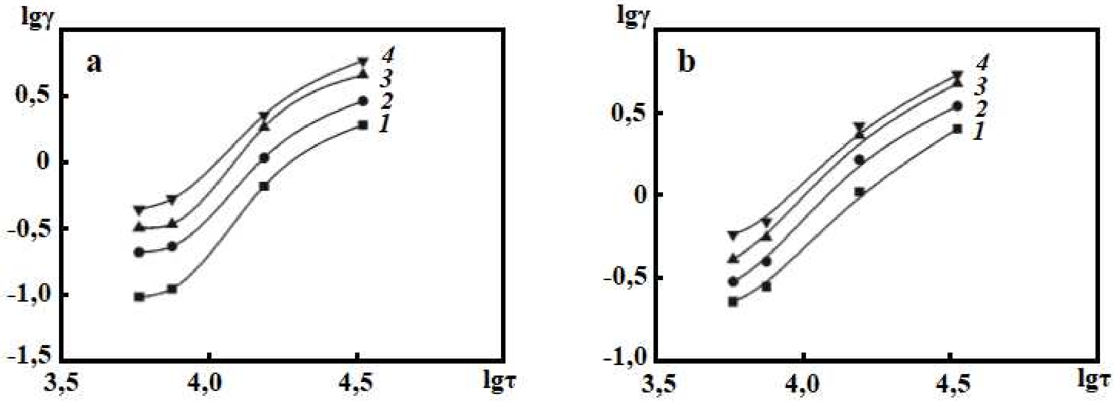

Figure 1. Flow curves of: a - initial random polypropylene, b - random polypropylene filled with 10 wt.% clinoptilolite, in logarithmic coordinates at temperature: 1 - 190° ; 2 - 210°C; 3 - 230°C; 4 - 250 °C

established on the flow curves of the filled composite (Fig. 1, b). There is reason to believe that the larger the size of aggregates of macrochains in the melt at relatively low temperatures, the more intensively their thermofluctuation decay begins with increasing temperature. Attention should be paid to one important fact, namely, that the introduction of 10 wt.% clinoptilolite in the composition of random polypropylene leads to an uneven change in the ratio of shear rates in comparison with the original random polypropylene. In the process of analyzing the flow curves of composites based on random polypropylene and 10 wt.% clinoptilolite, it becomes apparent that clinoptilolite, depending on temperature and shear stress, responds in a completely different way to the fluidity of the composite. So, for example, in the temperature range 190-210°C and $\lg\tau=3.77\text{-}3.88$, the melt flow rate of the composite is higher than that of random polypropylene. However, at a test temperature in the range of 230-250°C and $\lg\tau=4.19\text{-}4.52$, the melt shear rate of random polypropylene prevails over the flow rate of random polypropylene/clinoptilolite nanocomposite. The observed pattern in the change in melt flow in the random polypropylene/clinoptilolite nanocomposite indicates complex physicochemical processes occurring at the polymer-filler interface. In any case, it becomes obvious that the flow of the polymer melt in the uniaxial direction is a flow of primary structural formations – agglomerates, which can undergo certain structural transformations during thermo-mechanical action.

The flow of composites based on random polypropylene and clinoptilolite proceeds mainly in the non-Newtonian region, i.e. in the region where the effective melt viscosity depends on shear stress. Most likely, the arising anomaly of the melt viscosity depends on the intramolecular and intermolecular interactions at the polymer-filler interface. Under the action of shear stresses, macromolecules and their agglomerates, as well as agglomerates that arise at heterogeneous nucleation centers, are oriented along the direction of flow forces in the channel, thereby changing the microstructure and, accordingly, the melt viscosity. The region of greatest Newtonian viscosity corresponds to very small shear deformations. Under these flow conditions, no structural changes occur, and consequently, a change in the viscosity of the melt. Therefore, we believe that in the region of small shear rate gradients, the intensity of thermal motion of macromolecules is sufficient to interfere with the orientation of molecular coils and supramolecular formations. In this case, it is assumed that the polymer structure does not noticeably change, and the melt behaves like a Newtonian fluid. At high shear rates, the melt viscosity, having reached its lowest value, remains virtually unchanged. The fact of the existence of regions close to Newtonian on the flow curves does not in itself create any difficulties for the process of processing polymer nanocomposites, where the rheological factor is the determining technological parameter.

Studies of the temperature dependence of viscosity showed that for the initial random polypropylene, the apparent activation energy of the viscous flow is 33.5-88.3 kJ/mol, and for filled composites it varies from 46.0-48.0 kJ/mol.

The results of the study confirm the opinion that the rheological properties entirely depend on many factors, including structural features of the initial polymer matrix, type of filler, shear stress and melt temperature.

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