ON THE PLASTICIZATION OF FILLED POLYMERS

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Yu. S. Lipatov*

ON THE PLASTICIZATION OF FILLED POLYMERS

(Presented by Academician V. A. Kargin, 9 XII 1961)

Although a large number of works have been devoted to the study of plasticization processes (^{1,2}), to date, as far as we know, the phenomena of plasticization in filled polymers have not been investigated. In works carried out by the author and co-workers (^{3,4}), it was established that, when a polymer is filled, there occurs a noticeable change in the physicochemical properties of the polymer, due to adsorption interaction between bundles of molecules or any other secondary structures and the surface of the filler. From this point of view it seemed essential to clarify the influence of plasticizers on the properties of a filled polymer.

By the dilatometric method (^{5}) we investigated the glass-transition temperatures of polystyrene and polymethyl methacrylate films filled with glass powder and containing various amounts of plasticizer (dimethyl phthalate). Films of the filled polymers were prepared by casting from a solution of the polymer containing the required amount of plasticizer and suspended filler. The filler content in all experiments remained constant and amounted to 50% of the total weight of the filled polymer.

Figure 1 presents data on the dependence of the glass-transition temperatures of filled and unfilled polymers on the plasticizer content in volume percent. Filled polymers have higher glass-transition temperatures than unfilled ones, which is associated with a decrease in the mobility of chains and bundles as a result of interaction with the surface. The introduction of even a small amount of plasticizer leads to a sharp decrease in the glass-transition temperature of the polymers. At the same time, one and the same plasticizer content, as is seen from Fig. 1, causes a sharper decrease in the glass-transition temperature of the filled polymer than of the unfilled one.

It is significant that, when the plasticizer content in both polymers studied by us exceeds a certain limit, the glass-transition temperatures of the filled films become lower than those of the unfilled films. The intersection of the curves of the dependence of glass-transition temperature on plasticizer content for filled and unfilled polymers occurs at a lower plasticizer concentration for the less polar polystyrene. Figure 2 gives the dependences of the quantity Δt_g—the difference between the glass-transition temperatures of the unplasticized and plasticized polymer—on plasticizer content for filled and unfilled films.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The data shown in Fig. 2 demonstrate quite clearly that the introduction of plasticizer leads to a more substantial lowering of the glass-transition temperatures of filled polymers. On the basis of the concepts of interbundle plasticization developed in the work of V. A. Kargin and co-workers (6), and of the concepts concerning the nature of the interaction of polymers and fillers developed by us earlier (4), the data obtained may be explained as follows.

* Ya. P. Vasilenko took part in the experimental work.

The increase in the glass-transition temperatures of filled polymers is determined by the restriction of the mobility of bundles near the surface due to adsorption interaction and steric hindrances.

In the course of formation of a polymer film in the presence of a filler, bundles formed in concentrated solutions, or any other secondary structures, become bound to the surface of the filler (7). It is quite evident that the presence of a plasticizer cannot prevent the phenomena of secondary structure formation in solutions. Consequently, the plasticizer is not distributed uniformly among all the polymer molecules, as was previously assumed when considering the mechanism of plasticization. In the case of a filled polymer, the interaction of bundles with the surface of the filler will to a certain extent hinder interaction of the surface with plasticizer molecules (competition for sites on the surface between polymer and plasticizer molecules, reducing the adsorption of bundles on the surface). As a result, bundles of chains interacting with the surface in the presence of a plasticizer will have greater mobility than the mobility of bundles in the absence of a plasticizer, or than the mobility of bundles in the presence of the same amount of plasticizer and in the absence of filler.

Fig. 1. Dependence of the glass-transition temperatures of filled and unfilled polymers on plasticizer content: 1 –filled polystyrene, 2 –unfilled polystyrene, 3 –filled polymethyl methacrylate, 4 –unfilled polymethyl methacrylate

Fig. 2. Dependence of the difference in glass-transition temperatures of unplasticized and plasticized polymer on plasticizer content for filled and unfilled specimens: 1 –filled polystyrene, 2 –unfilled polystyrene, 3 –filled polymethyl methacrylate, 4 –unfilled polymethyl methacrylate

It may be assumed that in the case of a filled polymer, where there is a sufficiently developed contact surface between the polymer molecules and the filler, the effects of disruption of the bonds of bundles with the surface, analogous to the effects of interbundle plasticization, will play a predominant role. Since it is precisely the bonds with the surface that lead to a sharp increase in the glass-transition temperature upon filling, disruption of these bonds should give an equally sharp decrease in the glass-transition temperature of the plasticized filled polymer. According to V. A. Kargin (6), a sharp drop in glass-transition temperatures at low plasticizer content indicates interbundle plasticization. As can be seen from Fig. 1, such a strong drop in the glass-transition temperatures was observed at low plasticizer content for both polymers investigated by us, but the magnitude of this effect is more noticeable for the filled polymers. Consequently, the effects of interbundle plasticization are expressed more markedly for filled polymers, which, as we showed earlier (4), are characterized by looser packing at the surface. From the data of Figs. 1 and 2

It can obviously be concluded that, as the content of plasticizer in the polymer increases, the role of plasticization at the polymer–filler-surface interface gradually diminishes, while the effects of plasticization of the polymer itself, i.e., disruption of intermolecular bonds in the polymer itself, begin to play a more substantial role. Since interaction of the polymer with the surface also occurs at a relatively high plasticizer content, further weakening of the bonds with the surface is superimposed on the actual plasticization of the polymer, and the overall decrease in the glass-transition temperature in the presence of filler, at an equimolecular plasticizer content, becomes greater than for the unfilled polymer. Consequently, the breaking of bonds between polymer molecules and the surface occurs in the presence of plasticizer gradually and takes place even at high plasticizer contents. Otherwise, after their disruption we would have no differences in the glass-transition temperatures of filled and unfilled polymers, and ordinary plasticization of a polymer not bound to the surface would be observed.

On the basis of the data obtained, we may conclude that the plasticization of filled polymers is determined by two effects: interfacial plasticization, caused by disruption of bonds of the polymer–surface type, and plasticization caused by the usual disruption of bonds of the polymer–polymer type. The presence of two mechanisms of action of the plasticizer in the plasticization of filled polymers is of substantial importance for their use and may make it possible to vary the mechanical properties of the polymer over wide ranges by selecting the amounts of filler and plasticizer.

Institute of General and Inorganic Chemistry
Academy of Sciences of the BSSR

Received
9 XII 1961

CITED LITERATURE

1. V. A. Kargin, G. L. Slonimskii, *Short Essays on the Physical Chemistry of Polymers*, Moscow, 1960.

2. S. A. Glikman, *Introduction to the Physical Chemistry of High Polymers*, Saratov, 1959.
3. Yu. S. Lipatov, G. M. Pavlyuchenko, *Vysokomolek. soed.*, 2, 1565 (1960).
4. Yu. S. Lipatov, *Dokl. AN BSSR*, 5, 69 (1961).
5. L. Marker, R. Early, *J. Polym. Sci.*, 38, 369 (1959).
6. V. A. Kargin, P. V. Kozlov, R. M. Asimova, L. I. Anan' eva, *DAN*, 135, 357 (1960).
7. Yu. S. Lipatov, L. M. Sergeeva, V. P. Maksimova, *Vysokomolek. soed.*, 2, 1569 (1960).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.