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Abstract

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EVALUATION OF THE NATURE OF PLASTICIZATION OF POLYVINYL CHLORIDE BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

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In works ([1], [2]) it was shown that in polymers, in particular in polyvinyl chloride (PVC), three different types of plasticization may occur: intracellular, intercellular, and intermediate. Their evaluation is usually carried out from the shift of the glass-transition temperature upon changing the concentration of the introduced plasticizer. It was established by one of us ([3]) that the nuclear magnetic resonance (N.M.R.) method can be used to study the effectiveness of intracellular plasticizers of PVC.

Table 1

Fractions of protons responsible for the narrow component in the N.M.R. signal in samples with intercellular plasticizers

Plasticizer content in the sample, wt. %	Fraction of protons responsible for the narrow component of the N.M.R. line	Fraction of protons in the sample belonging to the plasticizer
10 KM	0.16	0.17
35 KM	0.52	0.51
80 KM	0.74	0.88
15 Gl	0.15	0.19
40 Gl	0.44	0.38
60 Gl	0.62	0.65

In the present work an attempt was made to apply this method to the study of different types of plasticization of PVC. PVC of grade PF-4 was investigated. As intracellular plasticizers, dimethyl phthalate (DMP), dibutyl phthalate (DBP), and dioctyl sebacate (DOS) were used; as intercellular plasticizers—castor oil

(KM) and glycerin (Gl); and as an intermediate plasticizer—ethyl stearate (ES). Their percentage content in the samples was varied from 10 to 85 wt.%; introduction into the polymer was carried out by the method described in (^{2}).

The proton spin-spin relaxation times T_2 were measured on a serial N.M.R. nuclear relaxometer by the spin-echo method. N.M.R. absorption spectra were recorded on a laboratory spectrometer in the form of derivatives (^{3}). Measurements were carried out at room temperature; in the case of ES—at 45°C.

The dependence of T_2 on the concentration of plasticizer in the samples is shown in Fig. 1. It is seen from it that, for PVC plasticized with intracellular plasticizers, a very strong dependence of the spin-spin relaxation time on the plasticizer concentration is observed; in samples with KM and Gl it is weak. The absolute values of T_2 in polymers with an intracellular plasticizer vary from several hundred microseconds (minimum plasticizer concentrations) to hundreds of milliseconds (pure plasticizer), i.e., the changes amount to 2–3 orders of magnitude. With the same change in the content of intercellular plasticizers (from 10 to 100%), T_2 increases by only a factor of 1.5–2; for the intermediate plasticizer—ES—the change in T_2 is more significant.

The N.M.R. spectra recorded from samples plasticized with KM and Gl, at any concentrations, are two-component curves consisting of a narrow and a broad line. The half-width of the latter is 9-10 Oe, which coincides with the half-width of the line for pure

PVC [^4]. Data on the number of protons responsible for the narrow component of the NMR line and calculated by the method of Wilson and Pake [^5] are presented in Table 1. It is evident from it that the narrow component of the signal in compositions with intermolecular plasticizers is determined by the protons of the latter. Since the T_2 times for which the protons of the polymer itself are responsible, amounting to 5–7 μsec, lie beyond the capabilities of the relaxometer, it remains to assume that the measured T_2 values refer to the protons of the plasticizer.

The same two-component spectra are observed for samples containing no more than 30-40% intramicellar plasticizer. In compositions having plasticizer concentrations higher than those indicated, the NMR signal is a single, sufficiently narrow line, and the spin-echo method gives one spin-spin relaxation time. This apparently indicates that, in these samples, the T_2 is due to the protons both of the plasticizer and of the strongly devitrified PVC, with the mobility of the plasticizer protons playing the determining role. This is all the more plausible since it is known that the content of the indicated plasticizers in such amounts lowers the glass-transition temperature below room temperature [^6].

The form of the NMR signal obtained from a sample that is a two-component composition—a solid body (polymer) and a liquid (plasticizer)—depends on the nature of the bond between the molecules of the two phases. When the molecules of the liquid interact weakly with the solid phase, they retain their individual mobility and the NMR absorption curve will be two-component. If, however,

Fig. 1. Dependence of T_2 on the content of PVC plasticizers: 1 –KM, 2 –Gl, 3 –ES, 4 –DBP, 5 –DMP, 6 –DOS

Figure 1: Fig. 1. Dependence of T_2 on the content of PVC plasticizers: 1 –KM, 2 –Gl, 3 –ES, 4 –DBP, 5 –DMP, 6 –DOS

the plasticizer molecules are in stronger energetic interaction with the polymer molecules, then their mobility, and consequently also T_2, should fall sharply, and the absorption curve should broaden.

Fig. 1. Dependence of T_2 on the content of PVC plasticizers: 1 –KM, 2 –Gl, 3 –ES, 4 –DBP, 5 –DMP, 6 –DOS

Spectra of the first type are observed for compositions of PVC with intermolecular plasticizers. These results agree with the mechanism of the plasticizing action of these substances [^1]. The fact that T_2 depends only weakly on the content of intermolecular plasticizers in the system directly indicates a weak interaction of polymer molecules with plasticizers of this type. The closeness of the T_2 values of pure KM and Gl and of PVC compositions with them indicates that the rigid macromolecules practically do not change the mobility of the plasticizer molecules, which apparently do not penetrate into the interior of the bundle but aggregate on its surface. The coincidence of the half-width values of the broad components in the spectrum of plasticized and pure PVC points to the same conclusion. The strong dependence of T_2 on the amount of intramicellar plasticizer introduced into the composition can be explained as follows.

If PVC has not yet been devitrified, then the absorption curve is two-component; at certain concentrations (30–40% for the plasticizers studied here) the polymer is devitrified, and the spectrum changes from two-component into a one-component, fairly narrow line, while T_2

of protons belonging to the polymer and the plasticizer increases sharply, tending toward the value of the spin-spin relaxation time of the pure plasticizer.

With the introduction of small concentrations of plasticizer, as a result of the strong energetic interaction of its molecules with the polymer molecules, the mobility of the plasticizer molecules decreases markedly. An increase in the amount of added plasticizer leads to an increase in the mobility of its molecules.

The mechanism of plasticization of PVC by ethyl stearate is intermediate, as indicated by the form of the dependence of T_2 on the plasticizer concentration.

Thus, the investigation carried out has shown the possibility of using the NMR method to evaluate the interaction of polymer and plasticizer molecules, while the nature of the concentration dependence of the spin-spin relaxation time of the protons in the sample makes it possible to establish the type of PVC plasticizer.

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