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Plasticizer Diffusion Into PVC Particles as Studied by ESR Spin Probe Method

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SUMMARY

The spin probe technique of electron spin resonance (ESR) spectroscopy has been applied for studying the plasticizer diffusion, migration, and redistribution processes in suspension polymerized PVC particles. In the first series of experiments six PVC powder samples with different K values (58, 61, 64,67,70, and 72) were mixed with diisooctyl phthalate (DOP) containing 10^{-4} M 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) as stable free radical spin probe. In the second run TEMPO-doped dry PVC powders were mixed with DOP plasticizer. Finally we studied the plasticizer transport phenomena between plasticized and non-plasticized polymer particles in powder mixtures. The observed diffusion properties of different samples were interpreted in terms of the different porosities of powders.

INTRODUCTION

The spin probe ESR technique has been extensively used in studying microstructure of synthetic polymers (1). Information of great theoretical and practical importance can be obtained by analysis of the ESR spectra of stable free radicals incorporated into condensed polymeric systems (2,3,4). The most commonly used spin probe species are of the nitroxide family and the majority of them belongs to the group of 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) derivatives. The theoretical background of interpretation of these spectra has been developed by Freed and coworkers (5,6). Since the ESR spectral data can be well correlated with molecular motions of spin probes being present in different media, it seems to be of interest to apply the spin probe method in order to investigate structural changes in the bulk of solid polymer particles due to the contact with plasticizing liquids.

It is also of practical importance to study the interactions between polymers and plasticizers as well as the subsequent structural changes. For example, many different methods have been applied for elucidating the mechanism of plastification (7,8), the plasticizer diffusion (10) and migration (11,12) in connection with PVC.

This communication is concerned with the application of the ESR spin probe method for the purpose of studying plasticizer redistribution in PVC/diisooctyl phthalate systems. The new experimental approach is based on the marked difference between the broad-line ESR spectra characteristic of the non-plasticized regions of TEMPO-doped PVC particles, and the motionally narrowed spectra corresponding to the plasticized domains.

EXPERIMENTAL

Suspension polymerized PVC powders with six different K values (58,61, 64,67,70 and 72) have been investigated. These materials have been produced by Borsod Chemical Work under the trade name Ongrovil S 5058,5061,5064,5067, 5070 and 5072, respectively.

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In the first series of experiments, PVC powders with K value 58 and 72, were mixed in a mortar at room temperature with different amounts (2,5,10,20, 30 and 40 w%) of diisooctyl phthalate (DOP) plasticizer containing 10^{-4} M dissolved 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO). Then the powders were placed in 5 mm OD glass ESR tubes, and the spectra were recorded immediately. Spectra were taken repeatedly for 90 days with samples stored at room temperature.

For the second test spin probe radicals had been incorporated into all of the six PVC samples prior to mixing them with the plasticizer. The incorporation was done by suspending 5 g PVC powder in 10 cm^3 benzene containing 10^{-3} M TEMPO. In order to obtain complete swelling the suspensions were kept for 24 hours at room temperature, then the solvent was carefully evaporated and the spin probed PVC samples were dryed in vacuo for 2 days. From the surface of dry particles, the TEMPO was removed by washing with methanol, and the sample was dried in vacuo. These pretreated powders were mixed with DOP in a mortar, and the ESR spectra were recorded similarly to the first series of experiments.

In order to study inter-particle liquid transfer, six PVC samples (K values: 58,61,64,67,70 and 72) containing 10 w% DOP were prepared: mixing was followed by heat treating (100 °C; 2 hours) in order to insure homogeneous distribution of the plasticizer. These plasticized powders were mixed with non-plasticized PVC powders containing TEMPO. The weight of PVC samples of various K values was 0.5 g in all cases.

ESR spectra were recorded with a JEOL-FE-3X spectrometer. Microwave power: 1 mW; modulation frequency: 100 kHz; modulation width: 0.1 mT; magnetic field range: 333 ± 5 mT. Precision of the temperature control was ±1°C.

RESULTS AND DISCUSSION

Plasticizer diffusion into the polymer

This process has been investigated by soaking the surface of PVC particles in DOP plasticizer, which contains dissolved TEMPO radicals (see Fig.1a).

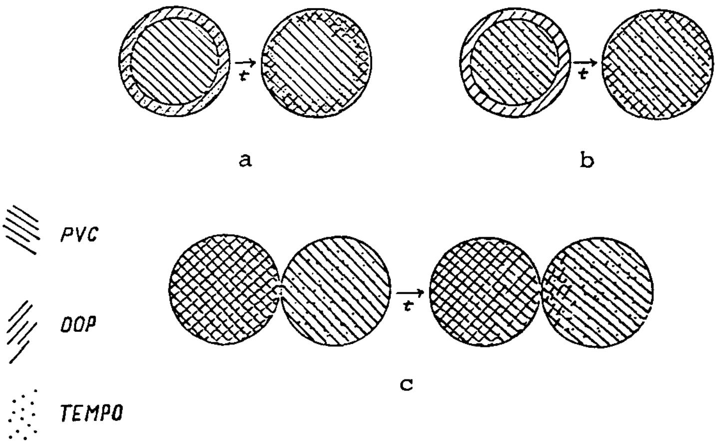

Figure 1: Schematic representation of the three experimental arrangements.

In diisooctyl phthalate solution the TEMPO radicals give the typical ESR spectrum, which consists of three lines with markedly different amplitudes due to the moderately fast molecular motion in viscous liquid media (Fig.2). From the L_1, L_2 and L_3 amplitudes and the width of the central line,

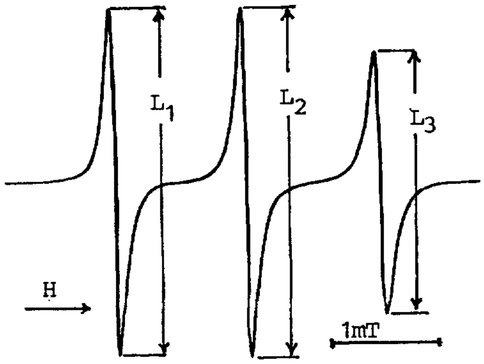

Figure 2: ESR spectrum of TEMPO radical dissolved in diisooctyl phthalate (recorded at room temperature).

one can calculate the correlation time of rotational diffusion of the spin probe molecule (13). Moreover, the amplitude ratio of second and third lines (L_2/L_3) also strongly depends on viscosity, or more specifically, on the probe mobility. As the process of filling the microcavities with plasticizer goes on, the rotational diffusion of spin probe becomes more hindered, which leads to increasing L_2/L_3 values.

Fig.3 shows the L_2/L_3 amplitude ratios for samples with K values 58 and 72, as recorded 10 minutes after mixing the PVC powder with different amounts of DOP. It can be seen from the plots that the lower is the amount of DOP in the mixture, the more hindered is the molecular motion of TEMPO. Naturally, Fig.3 does not represent an equilibrium situation, since homogeneous distribution of plasticizer cannot be reached within 10 minutes at room temperature. In the case of small amount of added plasticizer, the latter tends to form a liquid film on the surface of the internal cavities in PVC particles, where the degree of freedom of tumbing of TEMPO molecules is smaller than in liquids. At higher DOP concentrations, however, the cavities (pores) of larger size are also filled by DOP. In these microcompartments the spin probe species can tumble the same way as in bulk solution. After long storage significant restriction of mobility can be observed, which is due to the penetration of DOP into the smaller pores with size comparable to that of DOP and/or TEMPO molecules. At the initial stage of diffusion, however, the integrated amount of plasticizer enclosed in pores of small size is negligi-

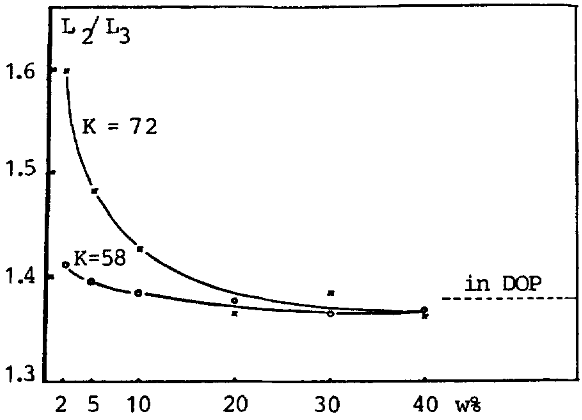

Figure 3: Amplitude ratios of spectra obtained with PVC powders containing increasing amount of DOP plasticizer. The spectra were taken at room temperature, 10 min after mixing.

ble with respect to that contained in large pores.

It can be seen from Fig.3 that the plasticizer-polymer interaction is more pronounced for samples with larger K values, if the spectra are taken immediately after mixing.

Plasticizer diffusion into PVC particles containing spin probe

The typical asymmetric broad spectrum (see Fig.4) characteristic of TEMPO immobilized in solid PVC particles undergoes significant changes as the plasticizer diffuses from the surface into the depth of polymer grains. As a result of several parallel processes (e.g. filling of pores and capillaries, adsorption on the internal surfaces, swelling, etc.) the plasticizer reaches larger and larger domains in the bulk volume. In those "flooded" areas the DOP dissolves the immobilized TEMPO molecules. At the same time the plasticizer looses the polymer matrix around the spin probe. This leads to superimposed spectra, where both the broad asymmetric triplet and the motionality narrowed "slow tumbling" triplet (Fig.5) can be clearly seen.

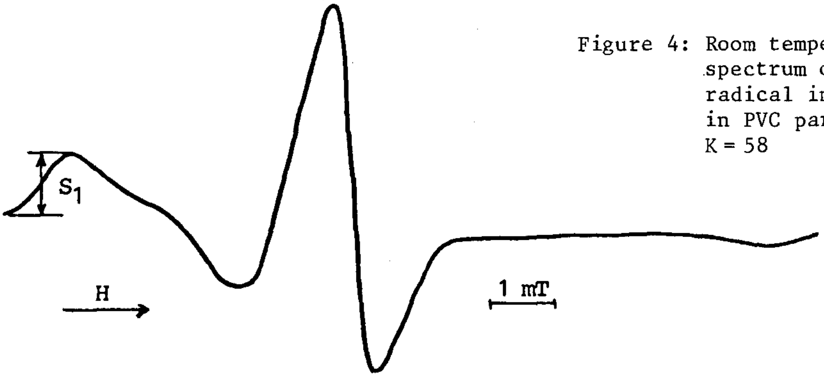

Figure 4: Room temperature ESR spectrum of TEMPO radical immobilized in PVC particles. K = 58

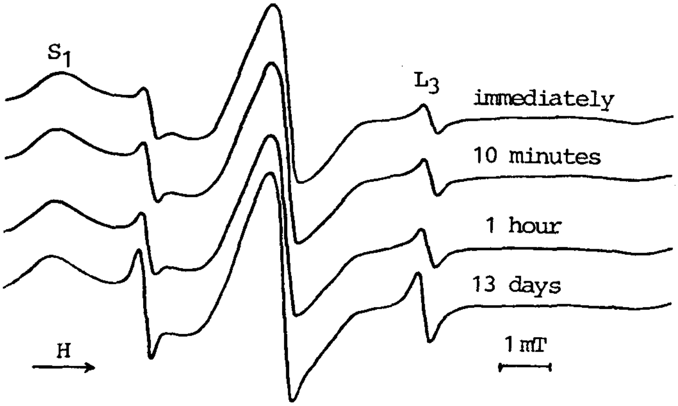

Figure 5: The dependence of superimposed (ESR) spectra recorded at room temperature. (2^{nd} series of experiments. K value: 58)

Since both the individual line widths and extremal separations of the component spectra differ markedly, the spectrum decomposition can be carried out, which affords to follow the process of DOP diffusion into the polymer particles. Fig.5 shows the superimposed spectra as a function of time.

Fig.6 shows the time dependence of the ratio of those lines of "liquid" and "solid" spectra that are well separated (i.e., the third and the first lines, respectively) for samples of all K values. It can be seen that for

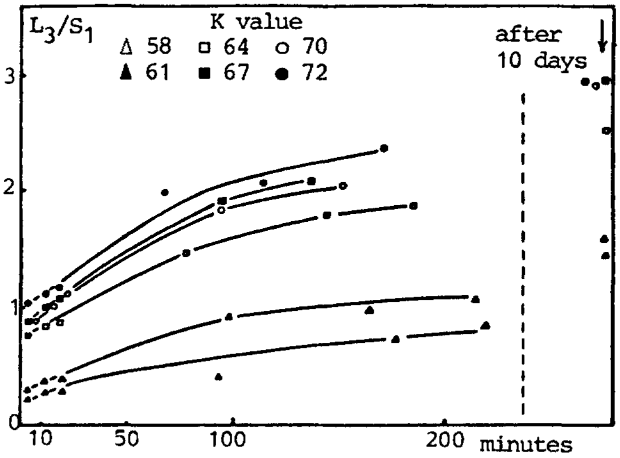

Figure 6: Time dependence of the L_3/L_1 ratio
t_0 = mixing time

samples of higher K values and diffusion rate is larger. The intensity ratios obtained after 10 days are given on the right side of Fig.6. The data recorded on subsequent days show only a minor increase. On the other hand, at the beginning of the diffusion process a rather fast build-up of the narrow triplet can be observed. In general, the curves of Fig.6 show an approximate $t^{1/2}$ dependence. As indicated in Fig.6, the PVC powders with K values 58 and 61 have a reduced tendency to take up plasticizer, whereas the powders with K values 67,70, and 72 have very similar behaviour resulting in a faster diffusion.

The K value dependence is not directly related to the molecular weight and structure, but to the morphology of powders. In particular, the porosity can play an important role in the diffusion process. In our case the six PVC samples under study have the following porosity values (14):

K value	58	61	64	67	70	72
Porosity (cm^3/g)	0.130	0.159	0.205	0.270	0.289	0.305

Fig.7 shows the correlation between the L_3/S_1 ratios measured after 10 days (see Fig.6) and the porosity values for all samples. Evidently, larger K values are associated with faster plasticizer diffusion (curve A).

Plasticizer transport between plasticized and non-plasticized PVC particles

The experimental arrangement is demonstrated in Fig.1c. In this case we have to take into account two simultaneous diffusion processes. First, the plasticized polymer particles tend to lose a part of their original DOP content, which leads to a new distribution of the liquid within the grains. When the DOP has large affinity for remaining in the bulk of particles, the "outward" diffusion (migration) is rather slow, particularly at lower DOP contents. As far as the DOP uptake of non-plasticized PVC particles is concerned, the equilibrium distribution of DOP can be established very slowly. Evidently, the area of contacting surfaces plays a very important role. Moreover, geometrical deformations may follow the swelling, that is why the modelling of these interparticle liquid transport phenomena seems to be a rather cumbersome task. ESR data, however, can give a deeper insight into the overall kinetics of these processes.

The superimposed spectra obtained immediately after mixing the two powders were similar to those shown in Fig.6.

Fig.7 shows the amplitude ratio of characteristic lines (L_3/S_1) ob-

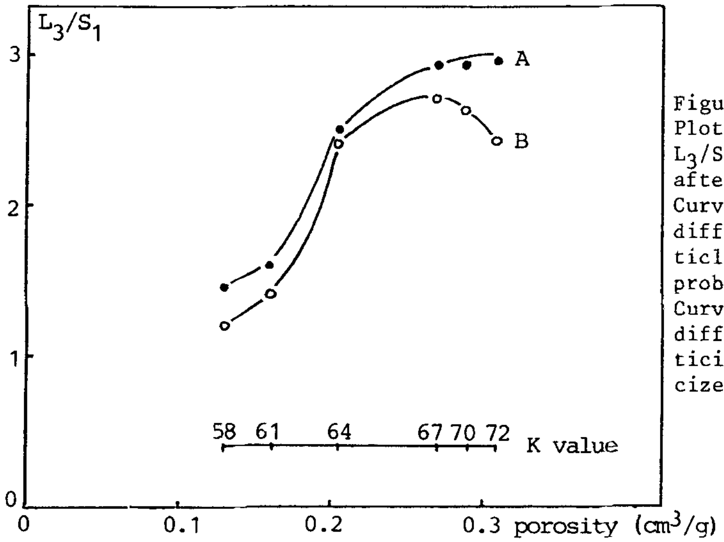

Figure 7:
Plot of porosity versus L_3/S_1 obtained 10 days after mixing.
Curve A: plasticizer diffusion into PVC particles containing spin probe.
Curve B: plasticizer diffusion between plasticizer and non-plasticizer PVC particles.

tained after 10 days. By comparing this plot (curve B) to that obtained in the previous experiment (curve A), we can see that while in the case of liquid-powder mixtures the rate of the DOP uptake by the non-plasticized PVC is a monotonously increasing function of the porosity (and of the K values as well), in the case of powder-powder mixtures an optimal K value can be found (K = 67), at which the rate of the interparticle DOP transfer is the largest.

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