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Electrical Conductivity in Doped Polyethylene

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Summary

Melt crystallized samples of mostly low density polyethylene were exposed to a bromine atmosphere, at room temperature, for long periods of time (3-30 h). The amount of absorbed halogen within the polymer increases with the increasing fraction of non crystalline material and decreases, while being stored in air, reaching a leveling off value. Concurrently the electrical conductivity is enhanced by several orders of magnitude depending on the proportion of absorbed dopant.

Introduction

Much attention has been given lately to the study of electrical properties of charge transfer complexes in polymers (KRYSZEWSKI, 1980). In particular, efforts have been made to develop a charge transfer mechanism in PE through adequate doping, aiming at an increase of conductivity. It is well known that bulk PE is characterized by stacks of lamellae (~10 nm) alternated by non-crystalline layers (chain folds, cilia, etc). Thus in order to participate in charge transfer electrons or holes must jump from a chain to a neighbouring one. However, transfer between chains is admittedly slow, leading to very low mobilities ($\sim 10^{-12} cm^2/vs$). A way to improve the mobility level is to dope PE with electron-donating molecules. In this case reaction occurs predominantly at the fold surface (BASSETT, 1964) (GUZMAN et al., 1980). The resulting mobility increase is not yet fully understood though the formation of a charge exchange complex has been suggested (KRYSZEWSKI, 1975).

The purpose of the present study is to examine the conductivity enhancement of melt crystallized doped PE. We report some preliminary experiments on the concurrent weight and conductivity variation after prolonged bromine exposure. Changes occurring as a function of storage time in a free atmosphere are examined. The influence of non-crystalline volume content on the conductivity level is emphasized.

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Experimental

The materials investigated were commercially available polyethylene samples mostly of the low density type supplied by Farbwerke Hoecht, BASF and Eastman (See Table I). According to the infrared analysis the branches attached to the main chain in these samples are butyl or longer methylene sequences (RUEDA, BALTA-CALLEJA and HIDALGO, 1979). The level of unsaturations (bands at 960 cm^{-1}, vinylene; 903 cm^{-1}, vinyl; 888 cm^{-1}, vinylidene) was previously characterized (RUEDA, BALTA-CALLEJA and HIDALGO, 1974)

TABLE I

Molecular weight, density and crystallinity derived from density, assuming ρ_a=880 Kg/m^3 for the investigated samples

Commercial Name	$M_w x10^{-3}$ (Kg/mol)	ρ (Kg/m^3)	α
Marlex 6015	150.0	962	0.72
Epolene C-11	20.5	994	0.60
Epolene N-10	21.8	926	0.47
Lupolene KR-1051	51.0	927	0.45
Lupolene KR-1032	15.7	920	0.41
Epolene C-13	285.0	911	0.32
Epolene C-10	20.9	904	0.26
Epolene C-12	11.0	897	0.20

Melt crystallized films about 500 μm thick with 2 cm diameter were exposed to bromine vapour at room temperature for periods between 3 and 30 hours. The relative weight increase values were derived from the weight of the samples before and after treatment. They are given as the ratio of the change in weight of the sample, Δp, to the weight of the sample before treatment p. For the conductivity measurements a Teflon-cell previously described was employed (VAQUERO and BALTA-CALLEJA 1977). The cross-section of the samples in contact with mercury was ~3 cm^2. An external voltage of ~$5x10^2$ V was applied accross the sample from a 246 keithly high voltage supply. The currents were measured at room temperature (20°C) after a time of 15 min with a Vibrating Reed Electrometer capable of detecting currents down to 10^{-15}Amp. The mercury for the electrodes was carefully replaced after each measurement.

Results and Discussion

Fig. 1 illustrates the linear dependence of the relative weight increase of doped polymer, after 210 min of bromine exposure, as a function of volume of non-crystalline material per unit weight, $(1-\alpha)\rho^{-1}$. In lamellar structures the latter value is proportional to the thickness of the interlamellar disordered layer (MARTINEZ SALAZAR, BALTA-CALLEJA, 1980). Thus the capability of the dopant to become incorporated into the polymer depends markedly on the volume of disordered material, capable to accommodate the foreing molecules. The highest bromine penetration reached in these experiments, $\Delta p/p \sim 17\%$, (measured after storing the sample, one day, in air) was given for the sample with largest crystallinity deficiency. The data of Fig. 1 show, in addition, that the amount of bromine absorbed is gradually removed while letting the samples stored at a free atmosphere. Hence, after two days storage, approximately 2/3 of the absorbed bromine escaped from the materials. For storage periods larger than 10 days a limiting value $(\Delta p/p)_o$ is reached. This leveling value, ascribed to the stable level of bromine left in the polymer, does not exceed, in these experiments, a 4%. The above data clearly suggest that only a minor fraction of dopant reacts with the polymer, probably at folds and other interlamellar defects. The fraction of bromine molecules per $10^2 CH_2$ which react with the polymer can be straightforwardly derived from the limiting value of $(\Delta p/p)_o$, from: $\varepsilon_{Br_2} = \rho^{-1}(\Delta p/p)_o\ (10^2 M_{CH_2}/M_{Br_2})$; M_{Br_2} and M_{CH_2} are the molecular weights of Br_2 and CH_2 respectively).

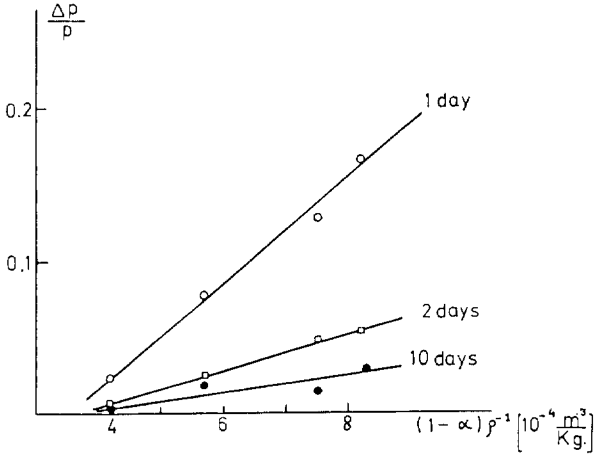

Fig. 1. Weight-increase of bromine-doped PE after 210 min as a function of non-crystalline volume content for different storage times.

The values obtained for ε_{Br_2} (Table II) show that the amount of dopant remaining within the polymer, after long storage times, is of the same order of magnitude as the level of unsaturated groups and one order of magnitude lower than the concentration of branches.

TABLE II

Comparison of bromine content ε_{Br_2} with unsaturation content, $\varepsilon_{c=c}$, and branching content for various samples.

Commercial Name	$\varepsilon_{Br_2}/10^2CH_2$	$\varepsilon_{c=c}/10^2CH_2$	$\varepsilon_{CH_3}/10^2CH_2$
Epolene C-10	0.38	0.093	4.68
Epolene N-10	0.19	0.058	2.80
Epolene C-13	0.15	0.066	3.54
Epolene C-11	0.018	0.000	1.21

More exactly, 1/3 of the dopant molecules react at unsaturated sites while 2/3 are reacting at other chain points (probably tertiary carbons atoms). The present results suggest that, for the conditions used, a major fraction of bromine penetrates in molecular form in the polymer diffusing gradually away thereafter, on storage. For samples with large crystallinities ($\alpha>0.7$), except for the low bromine level reacting $(\Delta p/p)_o$, the dopant is removed before 24 h.

We find that the films of PE show a substantial increase in electric conductivity when doped with bromine. Fig. 2 illustrates the typical conductivity enhancement measured immediately after doping, observed for a sample with $(1-\alpha)=0.55$ as a function of bromination time. Here $\sigma \sim 10^{-17} ohm^{-1}$. After 3-4 hours treatment the measured conductivity tends towards a characteristic saturation value. This limiting value of conductivity is undoubtedly connected with the maximum possible amount of Br_2 which can be accommodated in the non crystalline regions. Hence, we could systematically vary the conductivity of these PE films over a large range, by doping samples with varying non-crystalline contents. The increasing $(1-\alpha)$ values, localized mainly at the crystal surface, involve a rejection from the crystals of chain sequences containing an increasing number of defects (MARTINEZ SALAZAR and BALTA-CALLEJA, 1980). Fig. 3 shows the dramatic superlogaritmic increase of $\log \sigma_{BR}/\sigma$ after 15 h bromination, as a function of $(1-\alpha)\rho^{-1}$ over a range of seven orders of magnitude. Such a large increse might be tentatively ascribed to a conductivity mechanism involving an efficient char-

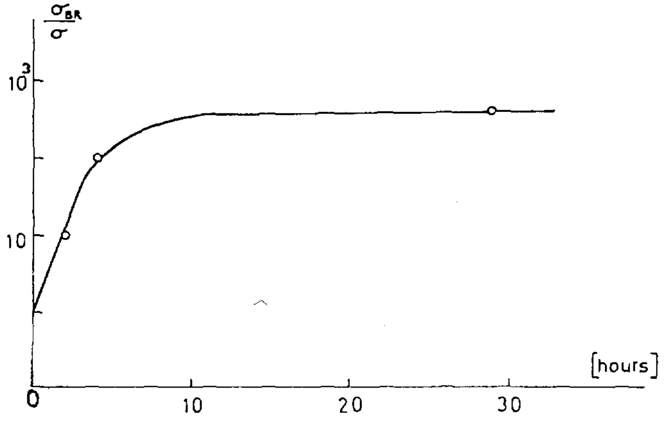

Fig. 2. Saturation of electrical conductivity increase as a function of exposure time to bromine, for the sample with $\alpha=0.45$

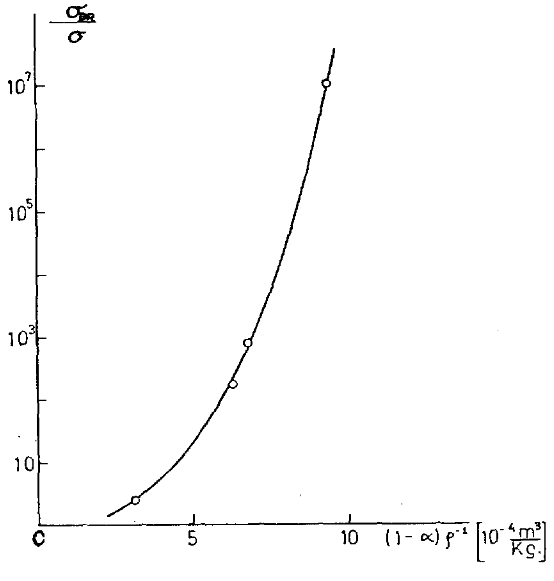

Fig. 3. Electrical conductivity increase of doped melt crystallized PE, referred to the initial value, as a function of non-crystalline volume-content. Treatment Time: 15 h.

ge transfer through bromine dopant occluded in the disordered regions of the polymer. When Δp/p reaches its limiting lowest value on storage, the level of conductivity increase lies, however, only within one order of magnitude. We have previously shown (RUEDA, BALTA-CALLEJA and HIDALGO, 1974) that the remaining bromine, after diffusion, indeed reacts with the unsaturated groups.

In summary, we have shown that doped polyethylene forms a type of material in which the electrical conductivity, measured shortly after doping can be varied over a range of several orders of magnitude. The conductivity level reached is a function of the weight of occluded dopant. Use of other dopants and doping conditions may improve the conductivity level and the stability of the dopant within the polymer.

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