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Comparison of NMR Investigation of Chemically Crosslinked Polyethylene and Polypropylene

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SUMMARY : Chemically crosslinked polyethylene and polypropylene were investigated by the means of NMR. Basing on this investigation the comparison of NMR relaxation times and structure of both polymers are made as a function of the concentration of the crosslinking agent.

INTRODUCTION

At the present state NMR investigation of the crosslinked polyethylene is focused mainly on the polyethylene crosslinked by irradiation. In this work we investigated chemically crosslinked PE. As far as the NMR investigation of the crosslinked polypropylene is concerned, we did not find any information on this subject in the literature. Also the comparison of NMR characteristics of both polyolefins as a function of the concentration of the crosslinking agent seems to be fruitful.

EXPERIMENTAL

Measurements have been performed by means of the pulse NMR spectrometer Brucker SXP4/100. We have evaluated the spin-spin relaxation time T_2, the spin-lattice relaxation time T_1, and the fraction of polymer with long and short relaxation times. The low density polyethylene with molecular weight 32000 was crosslinked with various amounts of dicumyl peroxide. The weight ratios of peroxide to polymer were 0.5, 1.0, 1.5, 2.0, 2.5. The same polyethylene was also crosslinked with other peroxides and the NMR results were similar to those presented for dicumyl peroxide (1,2). Details of the preparation of crosslinked PE and calculation of results are described in (1).
The crosslinked polypropylene was prepared by using the polymer with molecular weight 200 000. 1,4-bis (tert-butylperoxy)-diisopropylbenzene in the constant concentration 2 weight % and varying concentration of quinone as a coagent were used for crosslinking.

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The weight ratios of quinone to polypropylene were 0.5, 1.0, 1.5, 2.0, and 3.0. The preparation of the crosslinked polypropylene was described recently (3). The gel content between 70 and 90% (1,3) was obtained using the crosslinking compounds mentioned above.

RESULTS

1. The NMR results for crosslinked polyethylene

It was found that both crosslinked and uncrosslinked PE show two distinct spin-spin relaxation times T_2. One short time T_2' was attributed to crosslinks or entanglements as it was done in a similar work on irradiated PE (4). Long time T_2'' is attributed to the fraction of short chains or probably network defects in crosslinked PE. We have considered the T_2' as belonging to a phase called the hard amorphous phase of crosslinked PE and T_2'' subsequently to so called weak amorphous phase. Similar amorphous phases have been found in PE (5,6).
Figure 1 shows the time T_2' as a function of peroxide concentration at 25 and 45 °C. The 45°C is the relaxation temperature of crosslinked PE related to the motion in crystals of polymer, as it was established in (2). All values of T_2' at 25 °C are higher than the corresponding values for uncrosslinked PE. At 45 °C the situation is reversed. Two distinct extrema are observed in Fig. 1 at both temperatures, and they can be correlated to the extrema found in a dynamical mechanical investigation (1). These extrema are probably specific for this crosslinked PE. The first extrema of T_2' (Fig. 1, curve a and b) are in similar position as the maximum of crystallinity of crosslinked PE as a function of the peroxide concentration. These first T_2' extrema at both temperatures are correlated to the changes caused by crystals in the amorphous not very regular network of PE (1). At the temperature 45 °C (Fig. 1, curve b) all extrema are probably related to the changes of the amorphous phase in the vicinity of PE micelles. The second extrema at both temperatures show probably the regular and compact four-functional network in crosslinked PE (1), at 25 °C in some distance from crystals and at the 45 °C in the vicinity of PE crystals.
T_2'' as function of peroxide concentration at both temperatures tends to diminish gradually (Fig. 2, curves a and b). The extreme at 25 °C is difficult to explain. The dependence of the fraction with the short relaxation time "f" as a function of the peroxide concentration at both temperatures (Fig. 3, curves a and b) has a form like the above-mentioned T_2'' behaviour. Generally speaking there is a marked difference between the NMR characteristics measured in the rubber-like range of PE and in the α-relax-

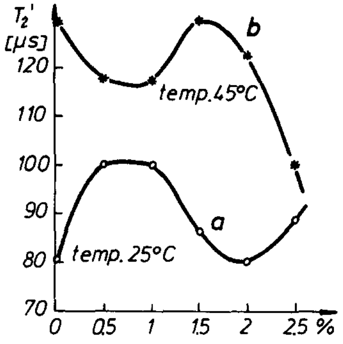

Fig. 1. Short spin-spin relaxation times T_2' of crosslinked polyethylene as a function of peroxide content at 25 and 45°C

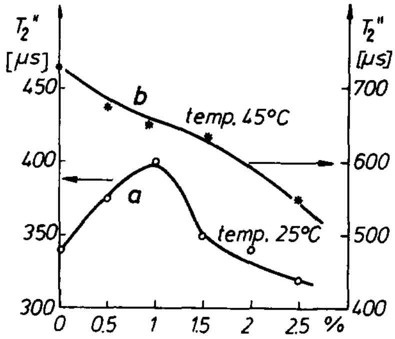

Fig. 2. Long spin-spin relaxation times T_2'' of crosslinked polyethylene as a function of peroxide content at 25 and 45°C

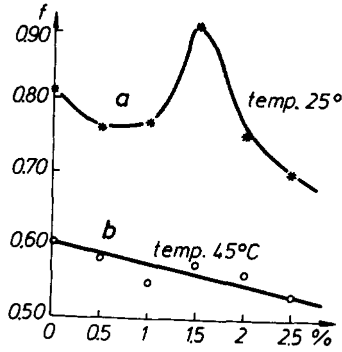

Fig. 3. The fraction with short relaxation time "f" of crosslinked PE as a function of peroxide amount at 25 and 45°C

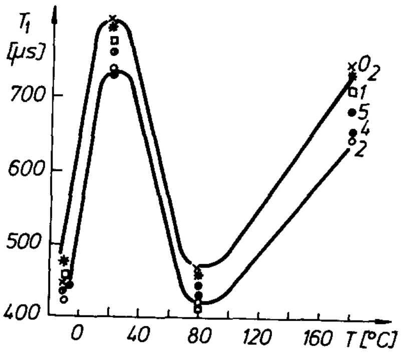

Fig. 4. Spin-lattice relaxation times T_1 of crosslinked PP (various amount of quinone, points 1-5) as function of temperature

ation range of PE where all processes seem to take place in crystals.

2. NMR results for crosslinked polypropylene

In Fig. 4 we can see the relation between the relaxation time T_1 and temperature for variously crosslinked PP. The crosslinked polypropylene has been studied at -15°C (glass-like state of polypropylene), 25°C (so called rubber-like state of crosslinked PP), 80°C where the α relaxation appears, and at 175°C (the melting temperature of PP). As is seen, values T_1 at -15°C and 80°C are similar. The same situation is observed at 25 and 175°C. From these relations we have drawn the conclusion that the T_1 time in PP and crosslinked PP is strongly dependent on free volume in these polymers.
The relation between time T_1 (at the above mentioned temperatures) and various concentrations of quinone are shown in Fig. 5. We can see that at -15 and 80°C the T_1 do not change remarkably with an increase of concentration of the quinone which corresponds to some extent to the density of the cross-bonds. On the contrary, at 25 and 175°C the relaxation time T_1 drops gradually with an increase of quinone concentration. Similarly, in the range of relatively big free volume (temp. 25 and 175°C), the increasing density of PP network strongly influences the time T_1. But in the state of small free volume (temp. -15 and 80°C) the PP network has no practical influence on the time T_1. Additionally, the different course of the dependence of the relaxation time T_1 on temperature in crosslinked PP strongly indicates different transition ranges in crosslinked and uncrosslinked PP. At -15 and 80°C, in glass-like state, and in crystalline state, the free volume is small and corresponding relaxation time is small, whereas at 25 and 175°C (rubber-like state and molten polymer) the free volume is big and relaxation time is also long.
The analysis of spin-spin relaxation time in uncrosslinked and slightly crosslinked PP (with 0.5% quinone) at -15°C (3) shows the existence of long and short spin-spin relaxation times and gives the fraction of material with the long relaxation time. When the concentration of quinone increases at this temperature, starting from 1% of this compound only one time T_2 is found. Probably in the range of very small free volume, the increasing volume of PP network is bonding physically in its structure the fraction of short PP chains making it impossible to separate the different phases responsible for the times T_2' and T_2''.
As is shown in Fig. 6, at higher temperatures (25 and 80°C) the relaxation times T_2' and T_2'' are very well pronounced. At 25°C (rubber-like state) the value of

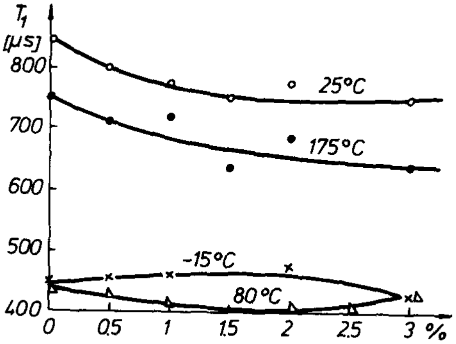

Fig. 5. Spin-lattice relaxation times T_1 of crosslinked PP at different temperatures as function of coagent content

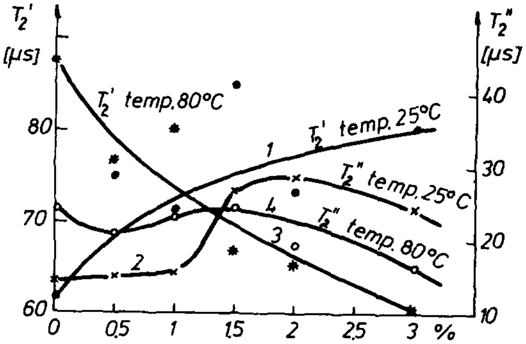

Fig. 6. Short and long spin-spin relaxation times T_2' and T_2'' of crosslinked PP at different temperatures as function of coagent content

the relaxation time T_2' increases with the increase of quinone concentration. This means that in spite of the increase of gel content (3) or network density, the density of the hard amorphous phase is diminishing steadily. The drop of the density of the hard amorphous phase at this temperature is explained by the behaviour of the fraction of material with the long relaxation time as a function of the quinone concentration (Fig. 7). In this Figure we can see that the amount of this fraction increases with the increase of quinone concentration. This probably means that the high concentration of quinone produces extensive degradation of PP chains and may indicate the appearence of substantial amounts of network defects. These effects are responsible for the decrease of hard phase density. The behaviour of T_2'' at this temperature (Fig. 6) is impossible to explain basing on our knowledge of crosslinkedPP structure (3). At the

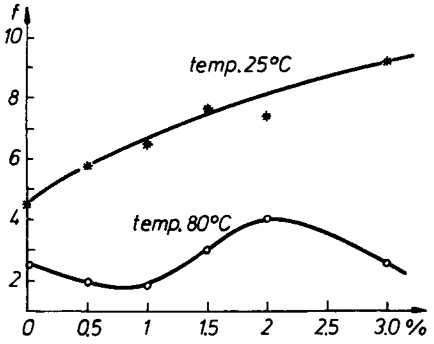

Fig. 7. The fraction with long relaxation time "f" of crosslinked PP at 25 and 80°C as function of coagent content

temperature 80°C (Fig. 6) the dependence of the relaxation time T_2' on quinone concentration is reversed to that measured at 25°C. The relaxation time T_2' does not change markedly with the increase of quinone concentration. Probably at α relaxation temperature where all processes seem to be concerned with PP crystals (low free volume), the amount of soft amorphous phase in the crystals does not increase. Simultaneously the increasing amount of PP network produces the increase of the density in the vicinity of crystals or in the PP micelle. The behaviour of T_2' at 80°C has the same shape as the "f" at 80°C (Fig. 7). This could be explained by the assumption that the crystallization following the crosslinking process in melt eliminates the soft amorphous phase. In the range of high crosslinking activation of quinone where the amount of gel is in its maximum and the crystallinity in the minimum, we have found that probably some kind of soft amorphous phase is built into the crystals (3). This causes changes in the

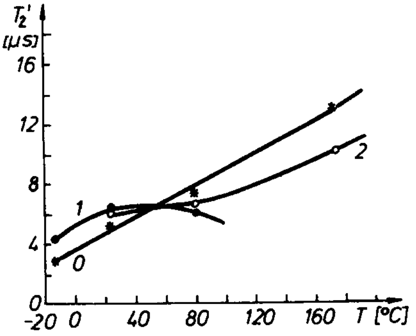

Fig. 8. The short spin-spin relaxation times T_2' for PP (0) and crosslinked PP (1,2) as function of temperature

unit cell dimensionand lowers the density what in consequence increases T_2' at about 1.5% of quinone (3). At this concentration of quinone we have found all the above described phenomena.
In Fig. 8 is shown the dependence of T_2' for some samples of crosslinked and uncrosslinked PP on temperature. As appears from these plots, the T_2' is sensitive to temperature to some extent.

CONCLUSION

1. In both crosslinked polymers two spin-spin relaxation times have been found, one short and another long. They can represent so-called hard and soft amorphous phase.
2. In both crosslinked polymers the value T_2' at 25°C is higher for crosslinked than for uncrosslinked polymer. The reversed situation is observed at the temperature of α relaxation of these polymers.
3. It seems that in both polymers the influence of networks and short chain phase on short and long spin-spin relaxation times is different and depends on the free volume of these polymers. At the relaxation temperature of these polymers all magnetic processes seem to be correlated with the behaviour of the crystals.
4. The spin-lattice relaxation times are probably very strongly dependent on the free volume of differently crosslinked PP and that of uncrosslinked PP. Moreover, the T_1 times do not change markedly when the amount of quinone increases and the free volume is small. However, in a state of relatively big free volume of crosslinked polypropylene, changes of this factor appear with the changes of amount of quinone.

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