Physico–mechanical investigation of crosslinked polypropylene

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We have investigated certain physical and mechanical properties of polypropylene that had been crosslinked with various amounts of quinone in the presence of a fixed amount of 1,4-ditertbutyloperoxy diisopropyl benzene. To achieve this we have used static and dynamic mechanical testing, X-ray, n.m.r. and gel fraction determination. Some correlation was obtained between these results.

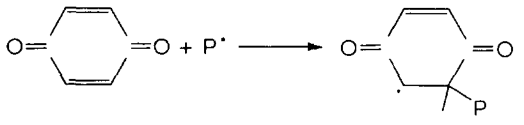
INTRODUCTION

This work is a continuation of our physico–mechanical investigations of XLPE and XLPP[1-4]. The method of crosslinking polypropylene with peroxide and a co-agent was intensively investigated by Chodak *et al.*[5,6], but we could not find any information about the physico–mechanical properties of XLPP.

Crosslinking of polypropylene by a radical mechanism is a complicated problem because of the rapid fragmentation of most of the macroradicals formed. The efficiency of the radical initiator is thus very low and an extraordinary large amount of peroxides are necessary for reaching the gel poing (e.g. ~8% dicumyl peroxide).

Another possibility is the use of a co-agent. The co-agent stabilizes polypropylene macro-radicals by the addition reaction of the polypropylene micro-radicals across a double bond of the monomer. The fragmentation of the macro-radicals is therefore retarded by this mechanism. A similar reaction of the next functional group leads to a crosslink being formed by the co-agent between two polymer chains. According to this idea the macro-radicals can be assumed to react with some other compound and also with the radicals themselves. On this basis we assumed the possibility of the polypropylene crosslinking being initiated by peroxide in the presence of quinone. The generation of the two radical centre in one molecule is suggested in these compounds.

The mechanism of action of the compound with the quinoid structure is not quite unambiguous. The possibility of forming relatively stable radicals must be taken into account. These stable radicals react with macro-radicals by recombination[4] or the reaction can be an addition of macro-radicals in the α position, as follows



Both reactions can take part in the two position of the molecule forming the cross-bond. In both cases the co-agent would be bound to the polymer[6].

Another possible mechanism is where the co-agent acts as typical stabilizer. This prevents the fragmentation of the macro-radicals by hydrogen transfer[6].

EXPERIMENTAL

Preparation of sample

The experiments were performed on isotactic polypropylene Tatren HFP (unstabilized product of Slovnafta–Bratislava, Czechoslovakia) with a molecular weight of about 200 000. It was crosslinked with a mixture of peroxide and co-agent. The peroxide was 1,4-ditertbutyl-peroxy diisopropyl benzene, and the co-agent was quinone. The propylene samples were prepared by inpregnating the polymer powder with the components added as a solution in benzene. After solvent evaporation the powder was mechanically homogenized and the samples were heated in a press at 160°C for 22 min[2].

We have used the components in the following weight percentages:

Table 1

Symbol of sample	0	1	2	3	4	5
Percent of peroxide	0	2	2	2	2	2
Percent of quinone	0	0.5	1	1.5	2	3

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Table 2 Interplanar distances in XLPP for three lines 110, 040, 130

Number of sample	110	040	130
0	6.15	5.16	4.70
1	6.15	5.17	4.71
2	6.24	5.22	4.76
3	6.26	5.25	4.77
4	6.24	5.22	4.77
5	6.13	5.16	4.67

Table 3 Ratio of the size of PP crystal in crosslinked PP to the size of crystal in uncrosslinked PP, perpendicular to the following direction 110, 040, 130

Number of sample	110	040	130
1	1.0	1.10	0.92
2	1.15	1.10	0.92
3	1.07	1.10	1.10
4	1.15	1.10	0.92
5	1.0	1.10	0.92

Gel fraction

The gel fraction was determined as the percentage weight of sample remaining after extraction in boiling xylene for 4 h with the addition of hydroquinone as a stabilizer. Prior to this extraction the samples were boiled in benzene to remove the atactic fraction of PP.

X-ray testing

The X-ray testing were performed with a cylindrical camera of radius 114 mm, with the CuKα radiation, filtered with Ni foil. For the investigations we used foils. Those techniques have been detailed previously[2]. In *Tables 2* and *3* we have presented the values of the interplanar distances, and the sizes of crystals.

N.m.r. investigation

The n.m.r. investigations were made in a pulse spectrometer Burker SXP4/100. We have calculated the spin–spin relaxation time T_2, spin–lattice relaxation time T_1 and the fraction of long relaxing time, f. Full information about applied method of testing and calculations have been detailed elsewhere[2,4].

Static mechanical testing

The investigations were made in an Instron machine type TT-CM with the strain rate $v = 1.0$ cm min^{-1}. Full information about this type of investigation can be obtained where[2] the following parameters were calculated from this testing: Young's modulus, yield point, the percentage of relative elongation at the yield point and the tensile strength.

Dynamical mechanical testing

(i) The torsion pendulum was used for dynamical testing in the range of temperatures from 220K to 430K. The range of frequencies were from 0.3 to 1.9 Hz. The calculation of storage modulus G' and the logarithmic decrement of attenuation were made according to formulas given previously[2].

(ii) The dynamical mechanical testing as a function of frequency have been made on a Weissenberg rheogoniometer type R-17. Calculation of the storage modulus has been made according to the Weissenberg equation[2].

RESULTS AND DISCUSSION

The dependence of the gel fraction on the quinone concentration shows a maximum in the range between 1% and 2% quinone concentration (see *Figure 1*). With a further increase in quinone concentration the gel content decreases.

This phenomenon can be simply explained by assuming that the excessive amount of quinone is leading to an ineffective decay of the initiator or alternatively it increases the degradation process in the polypropylene. A similar ineffective action in polypropylene crosslinked by quinone has been found by Chodak[6].

The degree of crystallinity dependence on quinone concentration, with a minimum at 1.5% quinone (see *Figure 2*) resembles a similar trend, as can be seen with

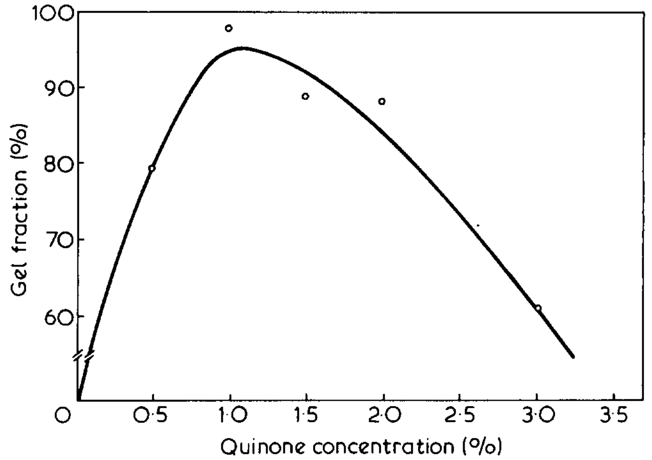

Figure 1 Dependence of gel fraction in XLPP on quinone concentration

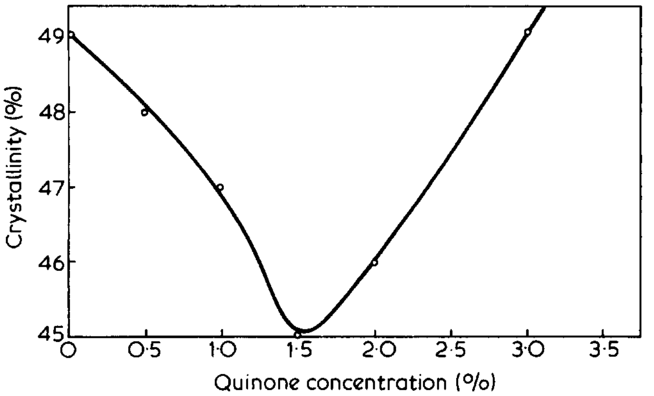

Figure 2 Dependence of crystallinity in XLPP on quinone concentration

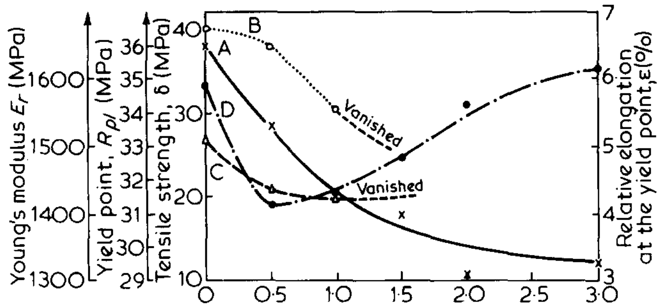

Figure 3 Dependence of Young's modulus – E_r, curve A; yield point – R_{pl}, curve B; tensile strength – curve C, and elongation at yield point- (%), curve D, as a quinone concentration

crosslinked PE[1]. Namely the increasing amount of gel diminishes the crystallinity.

From the X-ray investigation (see *Tables 2* and *3*) it could be seen that the differences in quinone concentration do not change the structural form of the crystals. However, the interplanar distance is bigger for samples 2, 3 and 4 than for the remaining samples. This could testify some changes in the unit cell of PP, demonstrated by the increase in the unit cell volume in the PP crystals. Some interpretation about the influence of crosslinks on the crystals and degree of crystallinity has been given by Mandelkern[7]. As far as the degree of crystallinity is concerned, crosslinks are eliminating chains from the crystallization process. We may add that as the crosslinking compound is not active for some unknown reason, producing a low crosslinking density, crystals from the molten state of XLPP could easily rebuild its structure after cooling. This produces some minor changes in the degree of crystallinity in comparison with the uncrosslinked material.

When the crosslinking compound is active (i.e. with maximum amount of gel) we assumed from our X-ray results that the increase in the unit cell volume is due to some imperfection within the crystal. There probably exists a less packaging effect in the crystals caused by part of the network built into the lamellae of PP. In the extreme case a very active crosslinking compound is changing the dimension of the unit cell of the crystals and retarding the crystallization process. In addition, from *Table 3* it can be seen that the maximum crystal sizes are produced by samples 2, 3 and 4, in the range where the quinone is very active. Diffraction lines 040 and 130 show practically no changes in crystal size.

The analysis of the static mechanical results show to some extent the same behaviour of XLPP as was encountered with XLPE[8]. Young's modulus, as a function of increasing amount of quinone, is decreasing (see *Figure 3*—curve A). The same phenomenon has been noted with XLPE. The variation of XLPP Young's modulus with changes in quinone concentration could not be attributed to the changes of crystallinity of XLPP, because changes in this phase are too small. Therefore we assumed that the Young's modulus in XLPP is dependent on the diminishing amount of short relaxing fraction[4]. A similar phenomenon has been observed in XLPE[5,8–10,12]. *Figure 12* shows the increase in the amount of *f* fraction with long relaxation time, but this means that the fraction of short relaxation time attributed to the, so called by us, hard amorphous phase is diminishing as a function of quinone concentration.

Yield point (*Figure 3*—curve B) and the elongation at the yield point, (*Figure 3*—curve D) at higher concentration of quinone disappear.

We could assume that the PP chains are crosslinked by some type of bridges consisting of quinone molecules. These bridges in this mode of mechanical movement do not plasticize the PP chains but are imposing the restraining effect on the sliding movements of PP chains under the applied stress. The restrain effects of quinone bridges on PP chain movements are probably greater than the plasticizing influence of the fraction of long relaxing time (*Figure 12*). Therefore the yield point disappears and the elongation is stable when the quinone concentration increases.

In crosslinked PE the plasticizing effect of crosslinking or the influence of fraction of long relaxation time was greater and the yield point drops slightly with increase in elongation at this point[8,9].

The tensile strength of XLPP as a function of quinone concentration (*Figure 3*—curve C) in the range of small quinone concentrations reveals a minimum and then increases. The tendency of these changes are similar to variations in crystallinity in XLPP. This correlation is similar to that for XLPE[1,3,8]. In this case we could say that the tensile strength is transmitted by the crystallinities not by amorphous phase. It is known that big stresses appearing at the breaking point of polymers are involved with the highly oriented amorphous phase or crystallinities.

The relation between storage modulus and temperature is of little interest, apart from showing the glass transition zone of XLPP between 260K to 280K[2]. More interesting information can be derived from the relation between the logarithmic decrement of attenuation and temperature (see *Figure 4*). The first maximum on these curves at −33°C is not described in the literature so far. The maximum at 7°C shows glass transition temperature, but the maximas in the range between 67°C and 97°C, which show the so called α_1 relaxation zones, related to the thermo-mechanical processes in PP crystals are more interesting but have not been fully investigated as yet.

The scattering of the α_1 relaxation temperatures for different samples is quite large, and could be attributed to some changes in PP crystals caused by crosslinking. More distinctly these processes could be traced to the relation

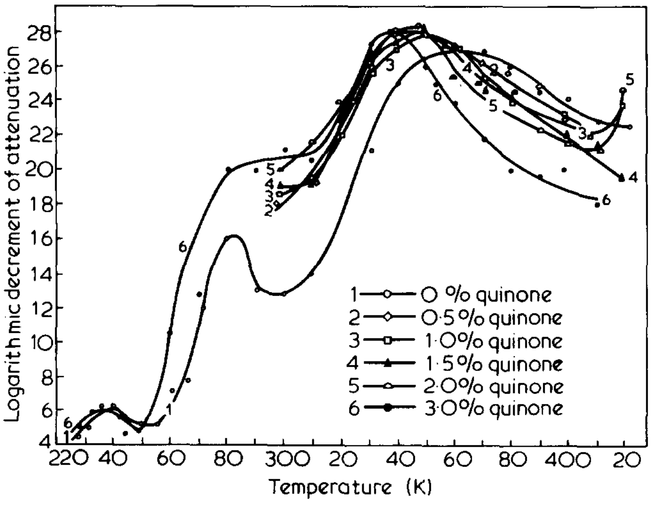

Figure 4 Dependence of logarithmic decrement of attenuation of XLPP on temperature

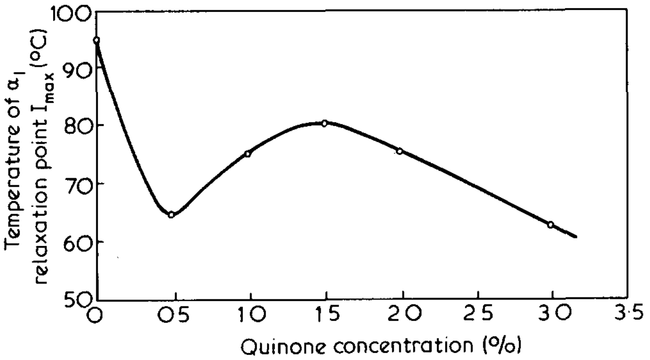

Figure 5 Dependence of temperatures of α_1 relaxation point of XLPP on quinone concentration

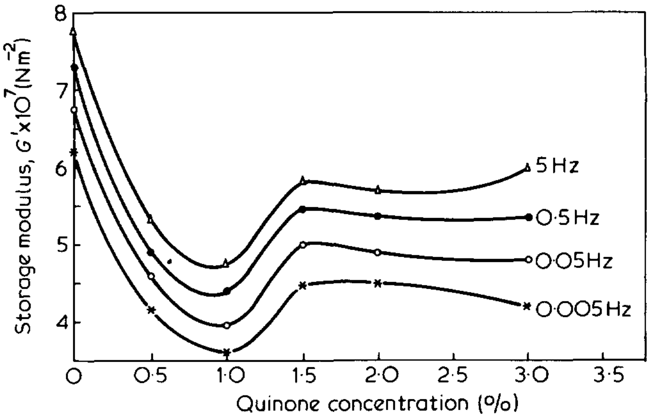

Figure 6 Dependence of storage modulus G' of XLPP at chosen frequencies on quinone concentration

between the maximal temperature at the α_1 relaxation point and the quinone concentration (see *Figure 5*). As could be seen from this Figure the value of T_{max} for XLPP is smaller than for uncrosslinked PP. A similar phenomenon was found for crosslinked PE[9,11]. Additionally, on this curve a small maximum in the range 1,5% of quinone concentration could be seen. Generally speaking the T_{max} in the function of crosslinking compound concentration is probably related to the amount of folds or lamellae as might be judged from the present investigation of XLPP, our investigation on XLPE[9,11] and other works[12]. Moreover in the range of 1,5% quinone concentration (high quinone activity of crosslinking and low crystallinity) crosslinking probably is, to some extent, taking place in crystals judging from the changes in crystal volumes.

From the Weissenberg measurement we have plotted the relation between storage modulus G' at a chosen frequency *versus* quinone concentration (*Figure 6*). It is necessary to emphasise that this dynamical deformation has been performed with low strain (200 μm) which probably means that the response of the material was in the linear viscoelastic range. The storage modulus of XLPP shows a lower value for this factor than for uncrosslinked PP.

This probably means that the PP chains crosslinked by quinone bridges are in this type of mechanical mode of deformation, plasticized by quinone bridges, lowering the dynamic stiffness of XLPP. the minimum of the curve $G' = f$(% quinone), in the range of 1% could be attributed, to some extent, to the maximum content of gel (see *Figure 6*).

There exists an analogy between the similar investigation on XLPE[9,11] and the above tested XLPP. In both cases, extremes of G' as a function of crosslinking compound concentration have been found. The further levelling off of this curve could be due to two factors. One: in this range of quinone concentration the gel content is diminishing, causing an increase in dynamical stiffness, two: the amount of long relaxing fraction, f, at 25°C (see *Figure 12*) increases, which would produce the plasticization effect and lower the stiffness of the XLPP.

In crosslinked and some uncrosslinked polymers[2,4,10,13], there appear two spin–spin relaxation times, one short T_2' which could be ascribed to the network or entanglement, representing as we call the hard amorphous phase in i.e. XLPE, and the long T_2'' ascribed to short chains and network defects which arise from the degradation processes. This phase we call, in XLPE, the soft amorphous phase[4]. Similar ideas were used in connection with PE[14,15].

Additionally we would like to point out that the selection of temperatures in these tests had the aim of finding out the behaviour of the n.m.r. factors that are characteristic for XLPP temperatures: −15°C (glass range of PP), 25°C (rubber range of PP), 80°C (α_1 relaxation range of PP), and 175°C (melting range of PP).

As we can see in *Figure 7*, distinct extrema of T_1 at all characteristic temperatures of XLPP appear. At −15°C and 80°C we have minima and alternatively at 25°C and 175°C we have maxima. These phenomena could be related to the size of the free volume in XLPP. In the glass-like state of XLPP and in crystals (α_1 relaxation range of XLPP) the values of free volume are comparable, the case is the same with the increased free volume in the rubber-like state of XLPP and in the melting state of this polymer.

At the temperature −15°C the time T_1 does not depend on the amount of the obtained network because we think the free volume is too small (see *Figure 8*—curve A). A similar phenomenon could be, to some extent, observed at 80°C (*Figure 8*—curve C). On the contrary, at 25°C where the free volume is relatively large, T_1 shows a steady drop

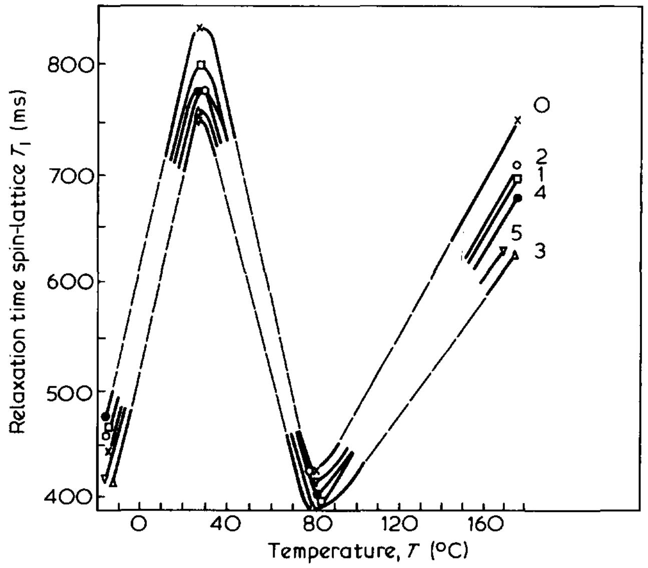

Figure 7 Dependence of relaxation time spin–lattice T_1 of XLPP on temperature. Number on curves indicate different samples of XLPP (see *Table 2*)

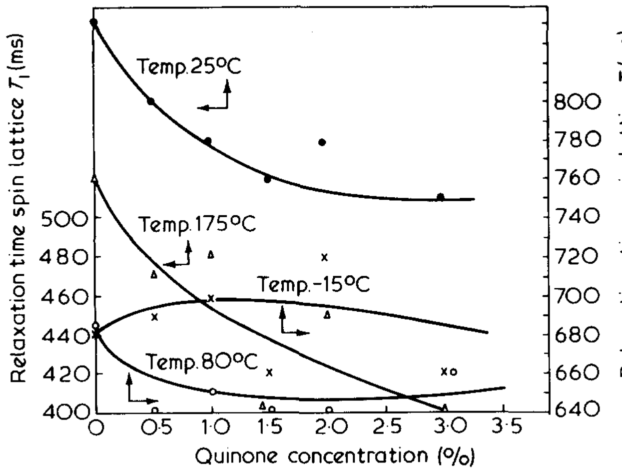

Figure 8 **Dependence of relaxation time spin–lattice T_1 of XLPP at different temperatures on quinone concentration**

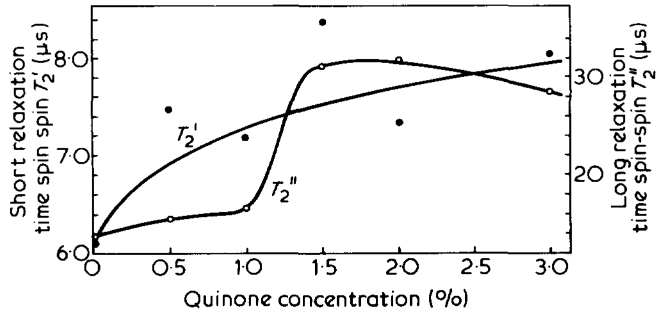

Figure 9 **Dependence of short relaxation time spin–spin T_2' and long relaxation time spin–spin T_2'' of XLPP at 25°C on quinone concentration**

with increase in quinone concentration (*Figure 8*—curve B). The same behaviour for T_1 can be observed at 175°C (*Figure 8*—curve D). From these observations we can draw the conclusion that the T_1 dependence on amount of network is closely related to the state of the free volume in this polymer.

The analysis of the relaxation time T_2 and fraction, *f*, of polymer with long relaxing time at temperature −15°C shows, for lightly crosslinked PP and uncrosslinked PP, classical short and long spin–spin relaxation times and the existence of fraction *f*. For the large concentration of quinone we found only one spin–spin time T_2.[13] In presence of a small free volume in PP or XLPP the increasing amount of crosslinks (network) are probably causing physical bonding of existing short chains fraction. The physical bonding concept of two different structures in a small free volume is probably the reason that the magnetic divisibility of these phases is cancelled.

At 25°C, because of the larger free volume the influence of soft and hard phase is more pronounced and two times T_2 (see *Figure 9*) appear. The noticeable increase in T_2' with the increasing quinone concentration could mean that, although this concentration increases, the density of the hard amorphous phase is dropping. This could be the reason why the values for Young's moduli as a function of quinone concentration diminish. Moreover it could be produced by the increase in the amount of degradation products and network defects, which is evident by the increase of the fraction *f* (see *Figure 12*).

The behaviour of the long relaxation time T_2'' at 25°C is difficult to explain.

The relation of T_2' and T_2'' as a function of quinone concentration at 80°C is shown in *Figure 10*. Generally speaking the T_2' gradually diminishes and the T_2'' does not change considerably. We are facing, here, a similar situation as for XLPE[5,9] at the temperature of the α relaxation.

In the rubber range of XLPP (25°C) the T_2' is increasing with increase in quinone concentration. At 80°C T_2' is decreasing with increase in quinone concentration.

This phenomenon could be explained, that in a very small free volume as it is in the lamellae of PP crystals, the influence of the fraction of long relaxation time is stable. The amount of this fraction does not increase in the lamellae as the concentration of the quinone increases (see *Figure 12*). This is partly the reason why the value for T_2' drops when the density of XLPP network increases, due to the steady proceeding of the crosslinking.

Comparing curves of T_2'' on *Figure 10* with the curve of *f* at 80°C (*Figure 12*), we can see that they are to some extent similar. During the crystallization process in the melt of XLPP, the long relaxing fraction or so called soft amorphous phase is eliminated. This process is well known in the crystallization of polymers.

One exception exists in the range for the very high crosslinking activity of quinone (i.e. 1% to 2% of this compound) where the long relaxing fraction penetrates the crystals causing a drop in their density and some increase in T_2'' (see *Figures 9* and *10*).

The results of n.m.r. testing T_2 at 175°C we obtained were so scattered that any interpretation was impossible.

In *Figure 11* the changes of T_2' with temperatures for some crosslinked samples of PP have been shown. As can be seen the T_2' increases slightly with increase in temperature, but T_2' is not so sensitive to the changes of

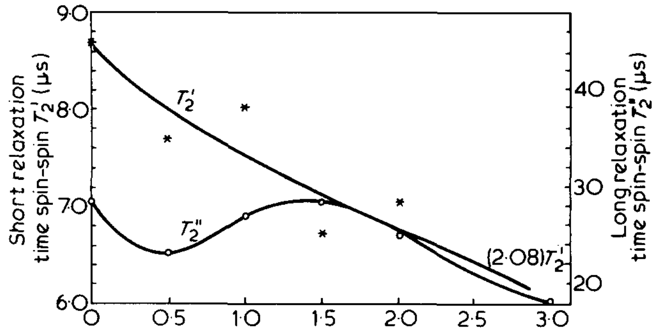

Figure 10 **Dependence of short relaxation time spin–spin T_2' and long relaxation time spin–spin T_2'' of XLPP at 80°C on quinone concentration**

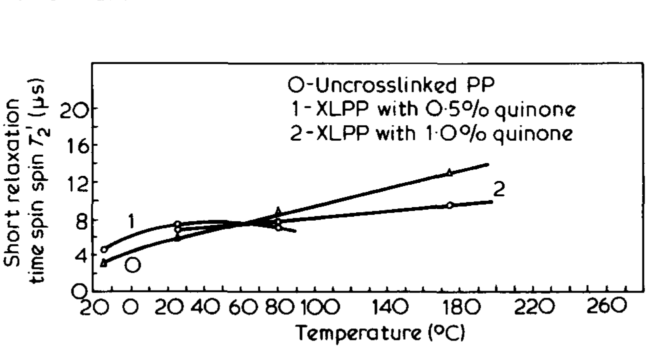

Figure 11 **Dependence of short relaxation time spin–spin T_2' for uncrosslinked PP and XLPP on temperature**

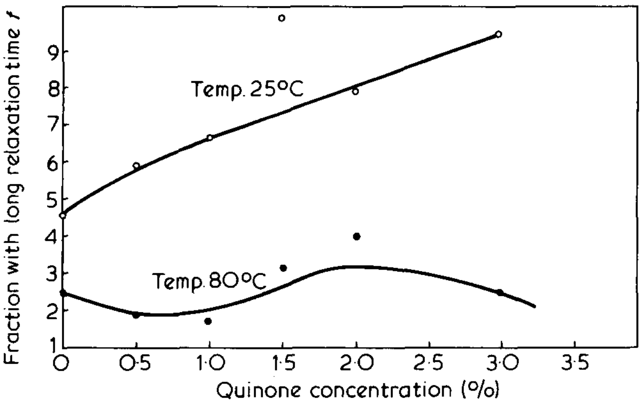

Figure 12 **Dependence of fraction with long relaxation time, *f*, of XLPP at 25°C and 80°C on quinone concentration**

this factor as the time T_1 is (see *Figure 8*). This phenomenon is well known for other polymers.

In *Figure 12* we have the relation between, *f*, and the quinone concentration at 25°C and 80°C, and these have been analysed in the above text.

CONCLUSIONS

(1) The properties of XLPP are to a certain degree similar to the chemically crosslinked low density PE[1,3,4].

(2) The crosslinking compound shows an activity optimum which causes appropriate changes in gel content, degree of crystallinity and even in the size of crystals.

(3) The static mechanical properties of XLPP are comparable to the properties of XLPE. In both cases the Young's moduli are diminishing as a function of increasing crosslinking compound concentration.

(4) The variation of attenuation in the α relaxation range proves that crosslinking is imposing some changes in the PP crystals. The variation of storage modulus shows that the quinone links are acting in this mode of deformation as a plasticizer.

(5) As a result of our n.m.r. investigations we could point out that in this polymer as in XLPE a hard and soft amorphous phase probably exist.

(6) The fraction of long relaxing polymer (soft phase), contrary to common thinking, is increasing and not decreasing when the crosslinking process is set in. The same situation is found for XLPE[4,10,13].

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