

Reactive melt processing of polyethylene: effect of peroxide action on polymer structure, melt rheology and relaxation behaviour

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(Revised 3 February 1997)

Reactive melt processing of polyethylene (PE) was accomplished at 170°C under the influence of two different doses (0.75 and 1.25 mmol per 100 g PE) of dicumyl peroxide (DCP). The effect of peroxide action on melt rheology of PE at 160, 180 and 190°C was studied by a constant shear rate plate and cone viscometer. Peroxide action led to establishment of a mild degree of crosslinkages in PE and hence to enhancement of its melt viscosity, the effect being higher for use of a higher DCP dose. The melts of PE and modified PE showed pseudoplastic flow behaviour. The pseudoplastic character, however was less pronounced at higher rates of shear and at a relatively low temperature. Use of a low dose of DCP (0.75 mmol per 100 g PE) modified the polymer marginally, causing little or only marginal changes in relaxation time and shear modulus, while a higher DCP dose (1.25 mmol per 100 g PE) incorporated significant changes in the polymer structure due to establishment of more than a critical degree of peroxide induced crosslinkages, thereby causing a substantial enhancement in the shear modulus and a drop in relaxation time. Odd effects of temperature on viscoelastic character are also interpreted on the basis of total dissolution of residual crystalline orientations in PE melts at $\geq 170^\circ\text{C}$. © 1997 Elsevier Science Ltd.

(Keywords: peroxide-action on polyethylene melt; crosslinking of polyethylene; reactive processing)

INTRODUCTION

Polyethylenes of different structural characteristics and rheological features^{1–4} are available on the market. Major contributing factors for the differences relate to selection of initiators of polymerization and other reaction conditions, including pressure, temperature and time of polymerization, mechanics involved and use of low molar proportions of a selected comonomer. Physical, mechanical and rheological properties of polyethylene (PE) are also reported to be substantially modified through blending with other polymers^{5–12} and by vinyl grafting^{7–11}. Vinyl grafting of PE is commonly achieved^{13,14} by its reactive melt processing in the presence of a selected monomer and a suitable peroxide initiator, usually under a good degree of shear action.

In this context, we thought it of interest to examine the nature and extent of modification of PE on shearing its melt in the presence of low doses of a peroxide with special reference to its melt rheology, viscoelastic character and relaxation phenomena. The present paper reports results of relevant studies on modification of low density polyethylene.

EXPERIMENTAL

Low density polyethylene, LDPE or simply PE (grade NCPE 4445 from Neste polyten AB, Sweden) having a density of 0.915 g ml⁻¹ and a melt flow index of 2.0 was used. Dicumyl peroxide (DCP) from Peroxide India Ltd was used as obtained.

Melt processing of PE with DCP

Known quantities of PE (60 g) and DCP (0.75 or 1.25 mmol per 100 g PE) were mixed together and milled in the shear mixer of a Brabender Plasticorder (Model PLE 330) employing a Cam type mixing head (N 50H) and using a rotor speed of 50 rpm for 25 min, at 170°C. Residual DCP was extracted out from each gross product using 1/1 mixture of benzene and tetrahydrofuran (THF) under reflux for 10 min. The residual polymer was then cooled, collected and dried in vacuum at 50°C.

Studies of melt rheology

Rheological characteristics of PE and peroxide treated PE were evaluated employing a constant shear rate technique on a rotational plate and cone (3° angle) viscometer (Rheotron 2744E from Brabender, Germany). A P10 plate and cone system was used in all measurements over the temperature range of 160–190°C

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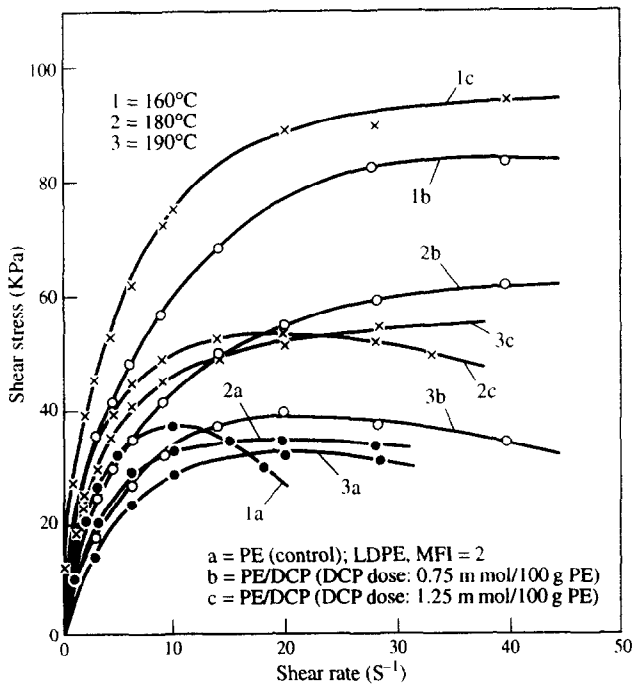


Figure 1 Effect of peroxide (DCP) action on melt rheology of polyethylene. Plot of shear stress (τ) vs shear rate (D) for PE and PE-DCP systems at different temperatures: 160, 180 and 190°C

at shear rates (D) of $0.1-56\text{ s}^{-1}$ using a sample size of $0.45 \pm 0.10\text{ g}$. Shear stress (τ) and shear viscosity (η) values corresponding to the applied shear rates were calculated out from data recorded or displayed using instrument constants. A time interval of 30 s was allowed between application of successive shear rates over the loading (increasing shear rate) and unloading (decreasing shear rate) cycle for measuring the corresponding shear stress and viscosity and assessments of short time thixotropy effect, Relaxation time (t_R) and shear modulus (G) of selected samples were obtained from measured values of shear stress developed at very low shear rates ($0.1-0.4\text{ s}^{-1}$), and following the decay of shear stress on withdrawal of shearing. We took the possible effect of polymer ejection from between the plate and cone of the rheometer, particularly at high rates, into account, and feel it to be negligible. The instrument manual also states that forcing out of excess material over the cone edge does not influence the measurement.

RESULTS AND DISCUSSION

Shearing of the PE melt in the shear mixer of Brabender Plasticorder using low DCP doses (0.75 and 1.25 mmol per 100 g PE) at 170°C for 25 min did not indicate a notable torque rise in the pasticorder recorder; the product obtained did not show a measurable gel content in boiling xylene. However, examination of the control PE and DCP-treated PE products in the precision plate and cone (rheotron) viscometer at selected high temperatures (160-190°C) under different shear rates points to some interesting features.

SHEAR STRESS (τ) VS SHEAR RATE (D)

Trends of variation in the development of shear stress (τ) on applications of different shear rates (D) at 160, 180

Table 1 Effect of Peroxide (DCP) action on melt rheology of PE

DCP dose (mmol per 100 g PE)	Temperature (°C)	Rupture parameters			Zero shear parameters				Flow behaviour index 'n'
		Rupture shear rate (s ⁻¹)	Rupture shear stress (kpa)	Rupture shear viscosity (kpa s)	Yield stress (kpa)	Zero shear viscosity (kpa s)	Degree of thixotropy (kpa s ⁻¹)	a	
0.00 (PE, control)	160	10.0	36.54	3.65	2.03	23.55	132.96	0.40	0.75
0.75	160	28.3	82.20	2.92	2.83	36.46	504.05	0.43	0.74
1.25	160	40.0	93.68	2.34	5.24	78.00	343.25	0.34	0.60
0.00 (PE, control)	180	20.0	34.85	1.74	1.20	13.05	210.53	0.46	0.80
0.75	180	28.3	61.13	2.00	1.50	19.16	370.39	0.50	0.77
1.25	180	40.0	53.76	1.34	3.35	46.07	200.56	0.40	0.62
0.00 (PE, control)	190	20.0	32.88	1.64	0.84	9.00	200.32	0.50	0.80
0.75	190	28.3	62.11	2.09	1.00	12.50	180.67	0.56	0.81
1.25	190	40.0	55.08	1.38	2.41	38.00	193.92	0.44	0.66

^a For higher shear rate zone
^b For lower shear rate zone

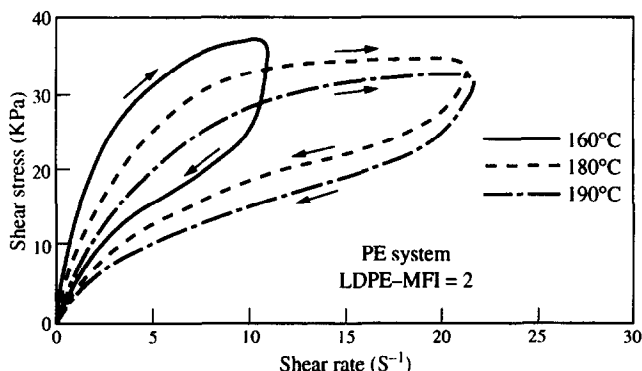


Figure 2 Thixotropic character of PE (LDPE, MFI = 2) at 160, 180 and 190°C. Plot of shear stress (τ) developed vs shear rate (D) applied over shear loading and unloading cycles in each case

and 190°C over the loading (ascending shear rate) cycle for the control PE and the PE-DCP products are shown in *Figure 1*. It may be seen that at a given temperature, the stress developed for application of a low shear rate was much higher in the PE-DCP system than in the control PE and that melt processing of PE with a higher DCP dose resulted in a notably higher enhancement in the observed stress level for application of a given shear rate. Also, shear stress developed for a given system under a given shear rate was lower for application of shear at a higher temperature according to common expectations.

RUPTURE OF STRUCTURE

For each of the PE and PE-DCP systems, the shear response over the loading (ascending shear rate) cycle at a given temperature was followed till the developed stress level just passed the maximum attainable value as indicated by the digital display of the Rheotron equipment. The state of the polymer just beyond the maximum stress level attained corresponded to inducement of rupture of the physical structure, i.e. shear-induced disentanglements of the polymer chains or segments thereof without, however, involving any chain scission due to shear action¹⁵. The critical shear rate at or beyond which the rupture happened is identified as the rupture shear rate (D_r) and the maximum shear stress level developed is taken as the rupture shear stress (τ_r). The τ_r and D_r values at a given temperature allowed calculation of rupture shear viscosity (η_r). Data for the observed and calculated rupture parameters for PE and PE-DCP systems are given in *Table 1*.

At a given temperature the rupture shear rates observed for the PE-DCP system are higher than the same for the control PE system. The rupture shear rate for the control PE gets substantially enhanced from 10 s^{-1} at 160°C to 20 s^{-1} at 180 and 190°C.

RESIDUAL CRYSTALLINE ORIENTATIONS AND THEIR DISAPPEARANCE

For PE melts a significant and critical structural change was reported¹⁶⁻¹⁸ to take place at a temperature of 160–168°C and this involved total dissolution of residual crystalline orientations in PE melt over the said temperature zone. Thus, inducement of a transformation in the pattern of order or (segmental/chain)

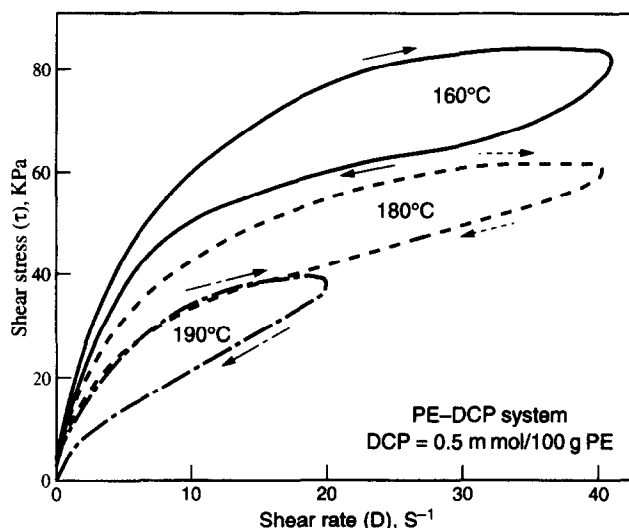


Figure 3 Thixotropic character of DCP treated PE (DCP dose = 0.75 mmol DCP per 100 g of PE) at 160, 180 and 190°C. Plot of shear stress (τ) developed vs shear rate (D) applied over shear loading and unloading cycles in each case

entanglements in the PE melt near or just above 170°C resulted in appearance of rupture of PE melt on application of a notably higher shear rate at 180 and 190°C than at 160°C. The enhanced stress level commonly developed in the DCP treated PE, *Figure 1*, compared to those developed in the control PE is viewed as a consequence of the enhanced degrees of immobilization of the PE chains or segments thereof, due to the microgel formation as a result of establishment of widely spaced peroxide-induced crosslinkages; this effect expectedly turned more contributing and effective for use of a higher peroxide (DCP) dose. Consequently, the PE-DCP system showed much higher rupture shear rates. The restricting effects of the variable degrees and distributions of traces of crosslinkages established in the PE chains for the use of two different doses of DCP (coupled with; (i) the total dissolution of the residual crystalline orientations in PE melt at temperatures $\geq 170^\circ\text{C}$ as stated above and (ii) the usual trend of thermal effects on viscoelastic behaviour) were manifested in a manner that did not show up notable differences in their observed rupture shear rates with variations in temperature of shearing, *Table 1*.

Melt rupture may be viewed as a phenomenon originating from stress concentration, which may be expected to be more severe in more highly entangled systems¹⁹. The rupture shear stress values are usually much higher for the DCP treated PE than for the control PE at each temperature of shearing. This indicates that the peroxide induced crosslinkages, however minor they might be, imparted overall structural changes that enabled the polymer melt to bear substantially higher shear stress levels before rupture.

RUPTURE SHEAR VISCOSITY (η_r) AND DEGREE OF THIXOTROPY

The rupture shear viscosity and the degree of thixotropy¹⁹⁻²¹ (area between the shear loading and shear unloading curves, *Figures 2 and 3*) for the control PE and PE-DCP systems are shown in *Table 1*. For the

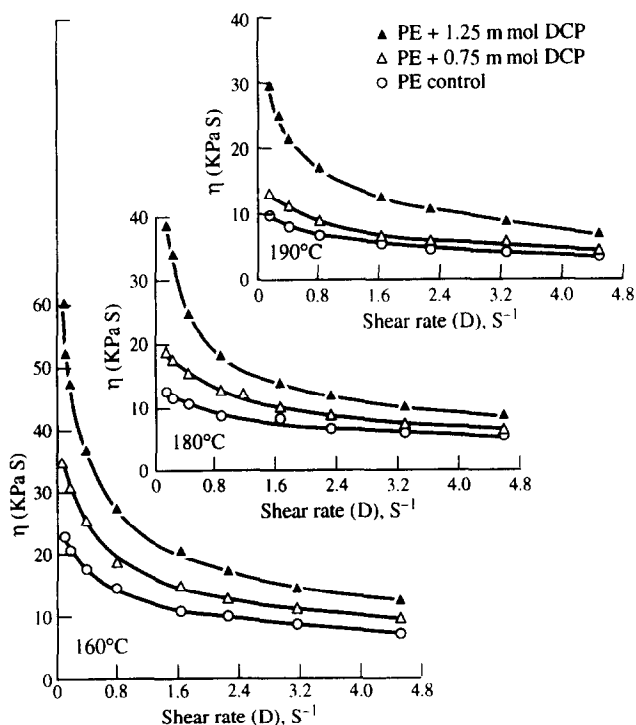


Figure 4 Plot of shear viscosity (η) vs shear rate (D) for PE and DCP treated PE at different temperatures

control PE, the thixotropy degree (the area of the thixotropic hysteresis loop, Figure 2) became higher as the melt was sheared at a higher temperature, while for the PE-DCP system (Figure 3), the trend was just the reverse. The complex nature of PE melt, the loss in the residual crystalline orientations in PE at or above 170°C, and the mobility-restraining effects of the established crosslinkages of uncontrolled distribution by the peroxide action, were contributing factors in determining the level of rupture viscosity and degree of thixotropy under the influence of different dose levels of peroxide (0.75–1.25 mmol per 100 g PE) and at different shearing temperature.

The pseudoplastic or shear thinning nature of PE and PE-DCP systems, and their variabilities with variation in temperature are shown as plots of shear viscosity (η_s) vs shear rates in Figure 4. The differences in the shear viscosities between PE and PE-DCP systems were found to narrow down at higher shear rates. The viscosity gradient with respect to shear rate applications commonly turned lower as the temperature of shearing increased. The values of zero shear stress and zero shear viscosity for the PE and the PE-DCP systems are shown in Table 1.

POWER LAW (FLOW BEHAVIOUR) INDEX

The simplest form of the power law equation relating shear stress (τ) and shear rate (D) may be written as

$$\tau = KD^n \quad (1)$$

or
$$\log \tau = \log K + n \log D \quad (2)$$

where n is the power law index, and K is a constant equal or equivalent to viscosity. Plots of $\log \tau$ vs $\log D$ for the control PE and PE-DCP system shown in Figure 5 allow determination of the power law index or flow behaviour index. Each plot describes two linear sections, one giving

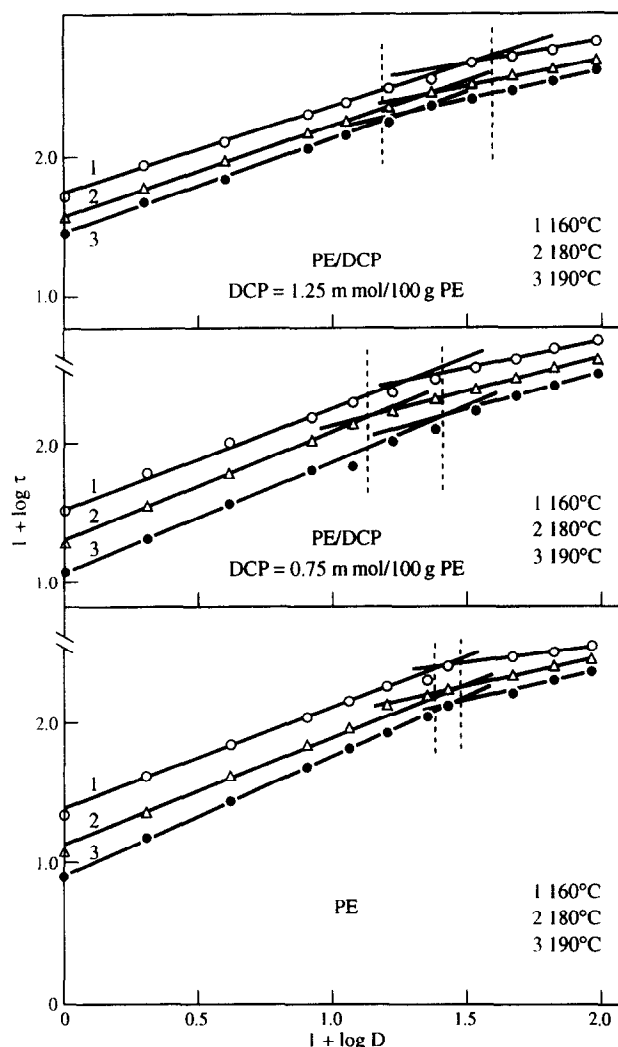


Figure 5 Effect of peroxide (DCP) action on melt flow behaviour of PE. Plot of $\log \tau$ vs $\log D$ for PE and DCP treated PE at 160, 180 and 190°C and evaluation of flow behaviour index (n value) given by the slope of the plots

a higher slope or n value over the low shear rate zone, and the other giving a relatively low slope or n value over the higher shear rate zone. The slopes are all less than unity, indicating pseudoplastic behaviour in each case, Table 1.

With an increase in shearing temperature, the pseudoplastic nature of melts of PE (unmodified or modified by peroxide action) becomes less prominent and the melt rheology tends to get closer to the Newtonian character (n -value becoming closer to unity). At a given temperature, PE modified with a higher DCP dose showed a higher degree of pseudoplasticity (i.e. lower n value). In the higher shear rate zone, modifications of PE with a low dose of DCP (0.75 mmol 100 g PE) appeared to slightly lower its pseudoplastic character, but the trend was reversed as the PE is modified using a relatively high dose of DCP (1.25 mmol per 100 g PE). It is difficult to find a simple explanation for the complex rheological patterns of PE and PE-DCP melts. The effects of residual crystalline orientations, which are reported to dissolve completely near or just above 170°C compared to those of shear action of different rates and different levels and odd distributions of mobility-restraining crosslinkages, established due to peroxide action, apparently combine

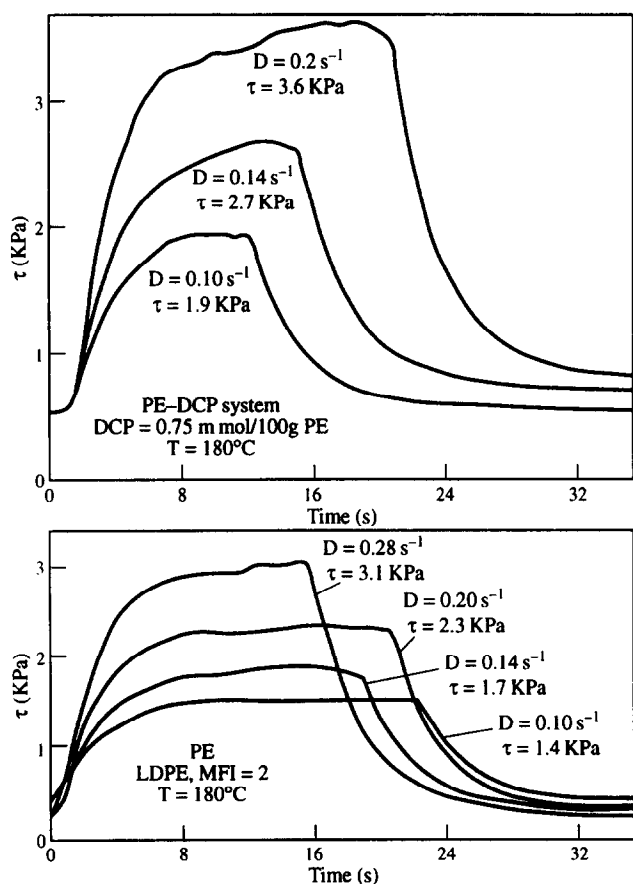


Figure 6 Selected relaxation curves showing decay of shear stress (τ) developed at selected low shear rates (D) applied on PE and DCP-treated (0.75 mmol DCP per 100 g PE) PE at 180°C

in a complex manner to ultimately determine the flow behaviour index or pseudoplastic character of PE and PE-DCP systems.

RELAXATION TIME (t_R) AND SHEAR MODULUS (G)

For the control PE and DCP-modified PE, the instantaneous maximum shear stress (τ_0) developed on application of a low shear rate (D) at a given temperature was allowed^{22–23} to decay on withdrawal of shearing. The time (t) required for the stress (τ) to decay to nearly 37%

$[(1/e) \times 100]$ of the corresponding maximum stress (τ_0), *Figure 6*, was taken as the relaxation time (t_R) according to the following relationship:

$$\tau = \tau_0 e^{-(\tau/\lambda)} \quad (3)$$

The term λ gives the relaxation time (t_R) at which $\tau = \tau_0/e$. The relaxation time (t_R) is taken^{24–25} as equal to η/G where G is the shear modulus and η is the viscosity corresponding to the stress whose decay is followed during relaxation.

The relaxation time (t_R) for the control PE and DCP modified PE suffers an initial, significant fall in its value with increasing shear rate over the low shear rate zone (0.1–0.28 s^{-1}) as in *Table 2*; however, a levelling off trend in the relaxation time with increase in shear rate beyond the initial region is a general feature much in tune with reported trends²⁶. The calculated shear modulus values over the said low shear rate zone remain practically unchanged, or change marginally for both control PE and PE modified with a low dose (0.75 mmol per 100 g PE) of DCP. However, for modification of PE using a high dose of DCP (1.25 mmol 100 g PE), the calculated shear modulus values at all the studied temperatures suffer significant changes as the shearing rate over the low shear rate zone is varied, as shown in *Table 2*.

As for analysis of combined effects of variation of DCP dose and of temperature of shearing, the observed trends with respect to relaxation time and shear modulus as shown in *Table 2* are far from uniform. However, it is clear that the change is usually negligible or marginal for modification of PE with a low DCP dose (0.75 mmol per 100 g PE), while it is measurable and significant for modification of PE using a high DCP dose (1.25 mmol per 100 g PE). The thermal effect on melt rheology and the effect of formation of microgels or crosslinkages (which becomes more prominent for use of a higher DCP dose) have opposing effects on the viscoelastic character of polymers such as PE, and its modified varieties. There is also the characteristic feature of total loss of residual crystalline orientation^{16–18} for PE near and above 170°C.

The odd trends in relaxation time and shear modulus values as in *Table 2* must be understood and interpreted in the light of the above odd factors influencing the viscoelastic character of the polymers studied.

The mechanism of chemical modification of PE during its reactive processing in presence of a peroxide (ROOR)

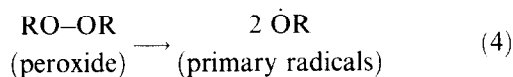
Table 2 Data for relaxation time (t_R) and shear modulus (G) at different shear rates applied at different temperatures for PE and DCP-treated PE

DCP dose (mmol per 100 g PE)	Temperature (°C)	Relaxation time, t_R (s)				Shear modulus, G (kPa)			
		t_{R1}	t_{R2}	t_{R3}	t_{R4}	G_1	G_2	G_3	G_4
0.00	160	2.2	1.9	1.7	1.4	13.41	14.17	14.53	16.13
0.75		2.0	1.8	1.6	1.4	14.00	14.00	14.5	16.00
1.25		2.0	1.3	1.2	1.1	14.00	19.81	19.82	20.67
0.00	180	2.0	1.8	1.6	1.5	9.48	9.20	9.07	8.86
0.75		2.0	1.9	1.8	1.7	8.31	8.40	8.45	8.33
1.25		1.4	0.8	0.8	0.7	28.10	44.71	43.91	40.57
0.00	190	1.4	1.4	1.3	1.25	6.35	6.36	6.39	6.48
0.75		1.6	1.45	1.3	1.20	10.68	10.49	9.81	9.54
1.25		1.4	0.7	0.7	0.7	39.04	36.63	33.10	30.11

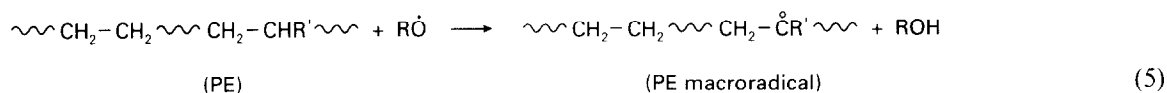
Suffixes 1, 2, 3 and 4 attached to relaxation time t_R and shear modulus G correspond to shear rates 0.1 s^{-1} , 0.14 g^{-1} , 0.20 s^{-1} and 0.28 s^{-1} respectively

can be depicted by the sequence of reactions shown below:

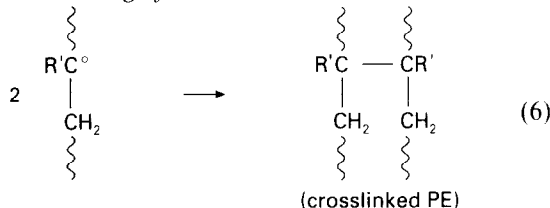
(a) Decomposition of peroxide to radicals



(b) Radical transfer to produce PE macroradial



(c) Crosslinking of PE:



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