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Dielectric Relaxation in Chlorinated Polyethylene–Polypropylene Copolymers*

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Abstract: Dielectric relaxation measurements were carried out on eight chlorinated polyethylene–polypropylene (PEPP) copolymers in the range of temperatures covering the main dielectric absorption. Chlorination of PEPP is expected to change the dynamic dielectric properties gradually with increasing amount of chlorine in the polymer chains. Thus, in the present study, increasing degrees of chlorination give a clear shift of the glass transition temperature towards higher values, except in the range between 40 and 51% chlorine, where an anomalous behaviour was observed. The same tendency is also observed in the relaxation strength ($\Delta\varepsilon$). The value of $\Delta\varepsilon$ has been estimated by using a non-linear squares regression program (LEVM6) to calculate the parameters of the Havriliak–Negami empirical equation. It appears reasonable to assume that the anomalous behaviour observed can be attributed to a compensation of the dipolar moments of chlorine groups in the macromolecules.

Key words: chlorinated polyethylene–polypropylene copolymers, dynamic dielectric properties, Fuoss–Kirkwood and Havriliak–Negami empirical equations.

INTRODUCTION

It is well known that the substitution of chlorine atoms in the polyolefins and polyvinylchloride leads to a considerable change of physical properties,[1,2] and also that the dielectric activity of non-polar polymers is increased by addition of polar groups. For example, polyethylene (PE) is rendered dielectrically active by introducing carbonyl ($\rangle$C=O) and chlorine (—Cl) groups in the chain.[3,4]

In the present work, we have studied the effect of addition of chlorine atoms on dielectric properties for a set of eight chlorinated polyethylene–polypropylene (PEPP) copolymers and have tried to correlate several characteristic parameters (e.g. glass transition temperature, T_g, relaxation intensity, position of dielectric loss peak) with the chlorine content. This system allows us to study the change of dynamic dielectric properties with increasing amount of chlorine in the polymer chains. Although it can be expected that chlorination of PEPP will gradually change the dielectric properties with chlorine content, it is possible that at certain levels of chlorine atoms, dipole–dipole interactions will become important and consequently the dielectric properties will reflect this fact.

For example, it is well known that the α peak relaxation can be correlated with T_g, and this parameter varies widely with structure and other parameters (e.g. intermolecular forces, intrachain steric hindrance, symmetrical substitution, bulky, rigid side groups). But the most important factor affecting T_g is chain flexibility, governed by the nature of the chemical groups which constitute the main chain. The incorporation of side groups on the main chain, which impede rotation and

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* The authors wish to dedicate this paper to Professor Günter Klar on the occasion of his 60th birthday.

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stiffen the chain, clearly cause a large increase in T_g. On the other hand, the presence of polar groups tends to raise T_g more than non-polar groups of equivalent size, because the polar interactions restrict rotation. According to this concept, with increasing degree of chlorination of PEPP copolymers, the T_g should rise, since the chains would be expected to become less flexible and the cohesive forces between the chains to become even stronger, when the number of dipoles (Cl atoms) on the polymer chains increases. Recently, Hößelbarth[2] has studied, by differential scanning calorimetry (DSC) measurements, the variation of T_g with increasing chlorine content for chlorinated polyethylene (PE-C) and chlorinated polyvinyl chloride (PVC-C), and found a continuous increase in T_g with the degree of chlorination in both cases.

EXPERIMENTAL

Preparation of polymers

The eight chlorinated ethylene and propylene copolymers were synthesized at 293 K in the presence of oligoazine of diacetyl without light irradiation. The degree of chlorination (percentage chlorine by mass), mass weight and the distribution of chlorine atoms on different groups are summarized in Table 1. The chlorination process, the molecular structure of these chlorinated samples and the distribution of chlorine atoms have been described in a previous paper.[5]

Dielectric measurements

Dielectric relaxation measurements by the conventional a.c. technique were carried out with a DEA 2970 equipment from TA Instruments at 20 frequencies over the range 10^{-1} to 10^5 Hz. The samples were moulded as disc-shaped pills of 1 mm thickness. The temperature ranges in each case were selected in order to cover the glass–rubber relaxation region. The frequency scans were taken at a heating rate of $1°C\,min^{-1}$.

RESULTS AND DISCUSSION

The temperature dependence of the dielectric loss ε'' for eight PEPP copolymers with different degrees of chlorination at 100 Hz is shown in Fig. 1. We can see in this plot that the position on the temperature axis of the loss peak shifts progressively to higher temperatures, except in the range of 40–51% chlorine content, where it is observed that the peak corresponding to the α relaxation passes through a maximum for 40% chlorine, decreases until the chlorine content is 51% and then increases again.

As an example, the imaginary part of the dielectric permittivity as a function of temperature at different frequencies and as a function of the frequency at different temperatures (in the range where the α relaxation

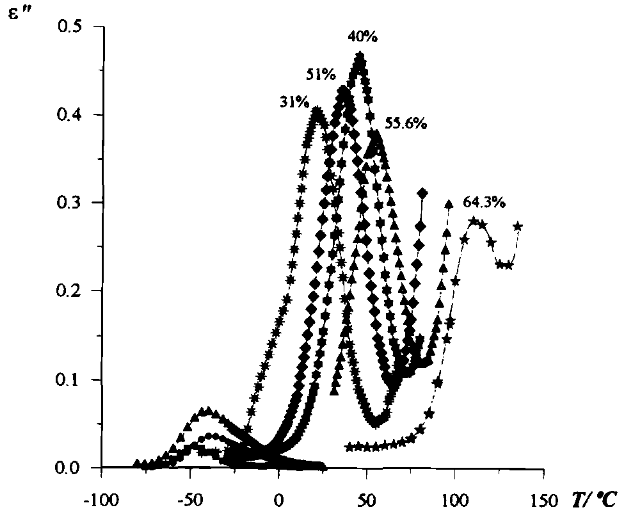

Fig. 1. Temperature dependence of the dielectric loss ε'' for eight chlorinated PEPP copolymers studied at 100 Hz: ■, 2·5% Cl; ●, 4·5% Cl; ▲, 6·5% Cl; other values are labelled.

TABLE 1. Chlorine content, molecular weight and distribution of Cl atoms on different groups for the eight chlorinated PEPP copolymers studied

	$\bar{M}_n$ $\bar{W}_n(g\,mol^{-1})$	Distribution of Cl atoms on different groups			
		$-CH_2Cl$	$=CH_2Cl$	CHCl	$-CHCl_2$
PEPP	29 000	0	0	0	0
PEPP 2·5% Cl	28 700	0·09	0·34	0	0
PEPP 4·5% Cl	29 300	0·17	0·62	0·1	0
PEPP 6·5% Cl	28 000	0·24	0·90	0·25	0
PEPP 31% Cl	29 400	1·16	6·20	1·40	0
PEPP 40% Cl	28 600	1·50	9·1	2·80	0·20
PEPP 51% Cl	27 800	2·70	12·3	2·80	0·20
PEPP 55·6% Cl	29 300	2·9	13·7	2·80	0·20
PEPP 64·3% Cl	28 500	3·3	13·7	2·80	1·30

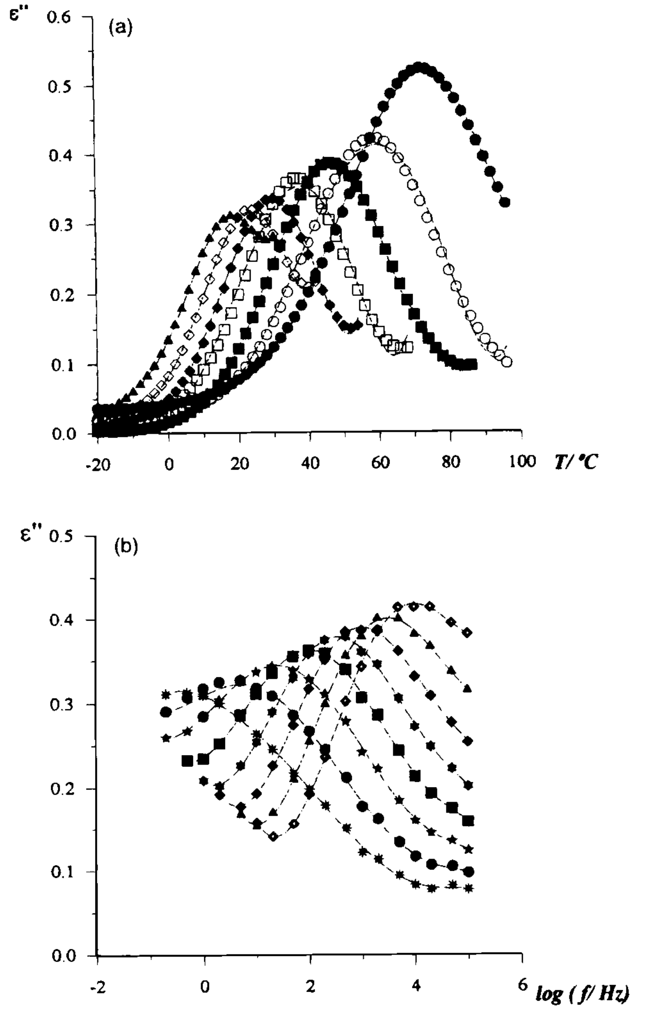

Fig. 2. Variation of the dielectric loss ε'' with (a) temperature at different frequencies (●, 10^5 Hz; ○, 10^4 Hz; ■, 10^3 Hz; □, 10^2 Hz; ◆, 10^1 Hz, ◇, 10^0 Hz; △ 10^{-1} Hz) and (b) frequency at different temperatures (✱, 20°C; ●, 25°C; ★, 30°C; ■, 35°C; ✳, 40°C; ◆, 45°C; △, 50°C; ◇, 55°C) for PEPP copolymer with a chlorine content of 51%.

occurs) for one of the PEPP copolymers studied is shown in Fig. 2.

In order to gain a better understanding of the observed behaviour of the variation of the temperature of the maximum of the loss peak (ε'') with the degree of chlorination of PEPP, we present in Fig. 3 the temperature of the loss peak (100 Hz) as a function of the chlorine content for the eight samples studied, as well as the corresponding values for polyvinyl chloride (PVC) and polyvinylidene chloride (PVDC) taken from the literature.[6]

To explain this peculiar behaviour, we have compared the experimental data for the α relaxation peak observed for each of the chlorinated PEPP copolymers with that assigned to other related polymers.[2,6] Thus, in spite of the increase in chlorine groups, the T_g for PVDC, 254·9 K, is about 98 K lower than the value of 353·6 K for PVC. According to Würstlin,[7] this differ-

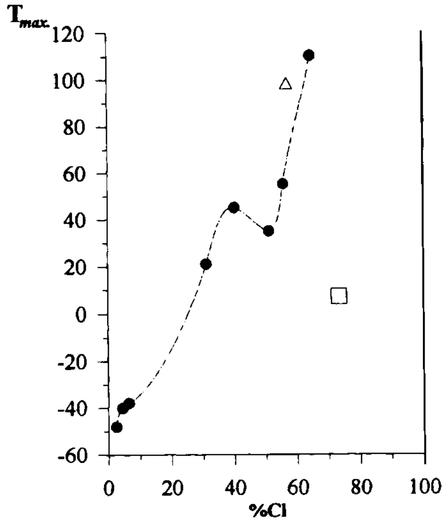

Fig. 3. Variation of the temperature of the maximum of the loss peak (ε'') with chlorine content for PEPP copolymers with 31, 40, 51 and 55·6% Cl, and other related polymers: △, PVC; □, PVDC.

TABLE 2. Values of the parameter *m* of the Fuoss–Kirkwood equation

	T (°C)	*m*
2·5% Cl	−50	0·401
	−40	0·417
	−30	0·437
4·5% Cl	−45	0·202
	−40	0·208
	−35	0·218
	−30	0·225
6·5% Cl	−50	0·235
	−45	0·238
	−40	0·245
	−35	0·249
	−30	0·251
31% Cl	15	0·228
	20	0·259
	25	0·287
	30	0·320
	35	0·339
	40	0·372
40% Cl	30	0·254
	35	0·264
	40	0·273
	45	0·319
	50	0·336
51% Cl	20	0·184
	25	0·197
	30	0·206
	35	0·219
	40	0·222
	45	0·253
	50	0·268
55·6% Cl	50	0·252
	55	0·275
	60	0·291
	65	0·317

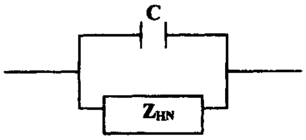

Fig. 4. Electrical circuit representing the dielectric process.

ence arises from the dipole–dipole interactions in the case of PVDC, owing to a partial compensation of the two C–Cl dipoles. However, a comparison with non-polar polyisobutylene (PIB, 202 K) or with other polar polymers such as polyvinylidene fluoride (PVDF, 238 K), polyvinyl fluoride (PVF, ~303 K) and polyvinyl bromide (PVBr, 373 K), suggests that steric factors may be largely involved. Hence, the T_g is about 50 K lower for PVF than for PVC. This difference probably arises from lower steric hindrances to main-chain rotations in the case of PVF, since the radius of fluorine is less than that of chlorine. Differences in polarity seen unlikely to be involved to a large extent, as evidenced by the fact that the dipole moment of CH_3Cl (1·87 D) is only slightly larger than that of CH_3F (1·81 D). Accordingly the anomalous behaviour observed could be related to a steric repulsion between groups of greater volume on alternate chain atoms, which is thought to lead to a distortion of main-chain valence angles.

Modelling of the relaxation peaks

It is interesting to fit the data to some empirical model in order to get information from the characteristic parameters of the model. Therefore, in our case the peaks were fitted to an empirical equation of the type:[8]

$$\varepsilon'' = \varepsilon''_{\max} \operatorname{sech} mx \qquad (1)$$

with $x = f_{\max}/f$, where $f_{\max}$ is the frequency at which the peak reaches a maximum and m ($0 < m < 1$) is a parameter dependent on temperature and frequency, which is related to the inter- and intra-molecular interactions among the relaxing species in such a way that the larger the parameter (unity is its maximum value), the lower are the interactions. The results, summarized in Table 2,

TABLE 3. Havriliak–Negami parameters ($\Delta\varepsilon$, ε_∞, α, γ, τ) for PEPP copolymers studied at different temperatures

	T (°C)	ε_∞	ε_0	$\Delta\varepsilon$	τ	α	γ
PEPP 2·5% Cl	−60	2·365	2·510	0·145			
	−50	2·362	2·487	0·125			
	−40	2·358	2·464	0·106			
	−30	2·355	2·44	0·085			
PEPP 4·5% Cl	−45	2·028	2·322	0·294	$2{\cdot}9520 \times 10^{-2}$	0·302	0·745
	−40	2·000	2·325	0·325	$4{\cdot}3566 \times 10^{-3}$	0·291	0·746
	−35	1·9532	2·3262	0·373	$5{\cdot}5771 \times 10^{-4}$	0·284	0·757
	−30	1·943	2·319	0·376	$1{\cdot}7145 \times 10^{-4}$	0·288	0·762
PEPP 6·5% Cl	−40	2·191	2·740	0·627	$1{\cdot}9838 \times 10^{-3}$	0·326	0·546
	−35	2·190	2·821	0·631	$4{\cdot}0034 \times 10^{-4}$	0·326	0·625
	−30	2·216	2·814	0·598	$1{\cdot}0206 \times 10^{-4}$	0·337	0·708
PEPP 31% Cl	20	2·622	5·547	2·925	$6{\cdot}2134 \times 10^{-3}$	0·402	0·600
	25	2·618	5·425	2·807	$1{\cdot}1206 \times 10^{-3}$	0·419	0·630
	30	2·603	5·295	2·692	$4{\cdot}2872 \times 10^{-3}$	0·480	0·540
	35	2·592	5·269	2·677	$1{\cdot}3323 \times 10^{-3}$	0·490	0·560
PEPP 40% Cl	35	2·711	5·724	3·014	$3{\cdot}7631 \times 10^{-2}$	0·380	0·800
	40	2·717	5·617	2·900	$6{\cdot}5175 \times 10^{-2}$	0·410	0·795
	45	2·728	5·588	2·860	$2{\cdot}0123 \times 10^{-3}$	0·440	0·730
	50	2·722	5·520	2·798	$8{\cdot}6870 \times 10^{-4}$	0·510	0·590
PEPP 51% Cl	25	2·475	5·401	2·926	$4{\cdot}9530 \times 10^{-1}$	0·393	0·436
	30	2·453	5·372	2·919	$6{\cdot}4639 \times 10^{-2}$	0·406	0·449
	35	2·432	5·340	2·908	$1{\cdot}1906 \times 10^{-2}$	0·416	0·473
	40	2·414	5·311	2·896	$2{\cdot}4816 \times 10^{-3}$	0·421	0·499
PEPP 55·6% Cl	50	2·616	5·204	2·588	$8{\cdot}8046 \times 10^{-3}$	0·380	0·765
	55	2·647	5·151	2·504	$2{\cdot}4890 \times 10^{-3}$	0·426	0·726
	60	2·651	5·081	2·430	$2{\cdot}6201 \times 10^{-4}$	0·440	0·700
	65	2·653	5·022	2·369	$2{\cdot}5660 \times 10^{-4}$	0·490	0·626
PEPP 64·3% Cl	100	2·295	4·097	1·798	$8{\cdot}84412 \times 10^{-2}$	0·614	0·219

$\Delta\varepsilon$ is relaxation strength

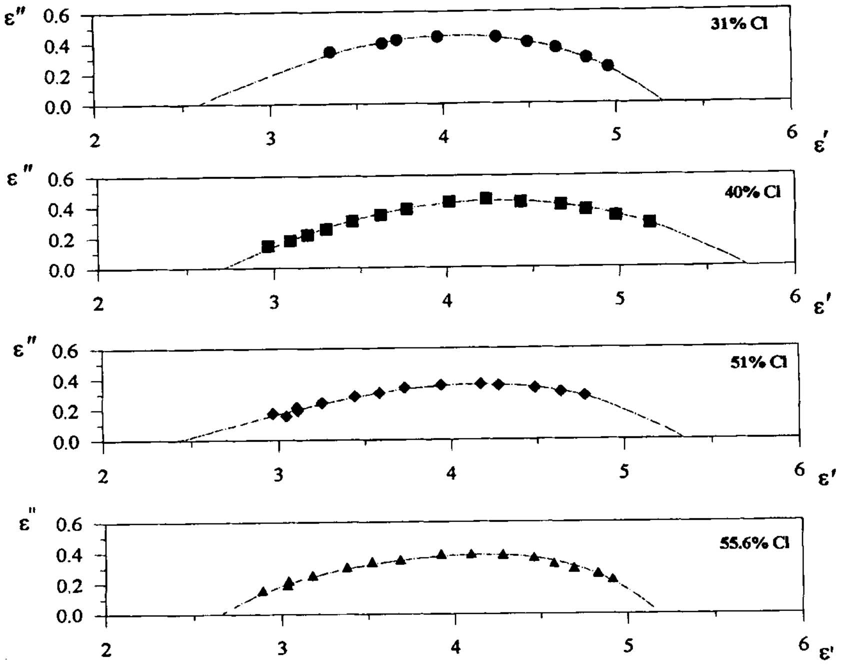

Fig. 5. Complex plane representation of PEPP copolymers with chlorine contents of 31, 40 and 51% at 35°C and 55·6% at 55°C.

suggest that the dipolar interactions are higher in PEPP copolymers with high chlorine contents, as a consequence of the higher concentration of dipoles per unit volume of the polymer.

In order to quantify more closely the dielectric relaxation processes, we represent them in terms of Cole–Cole plots, that is, a plot of ε'' against ε'. Whereas for Debye type peaks these plots are semicircles, the complex diagram plots representing the dielectric results associated with dielectric relaxation are skewed arcs. The curves are usually fitted by the Havriliak–Negami (HN) empirical equation;[9]

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (i\omega\tau_0)^\alpha]^\gamma} \qquad (2)$$

where ε_0 and ε_∞ are the relaxed and unrelaxed dielectric permittivity of the relaxation process, τ_0 is the central relaxation time, ω is the angular frequency and α and γ are parameters related to the shape and skewness of the

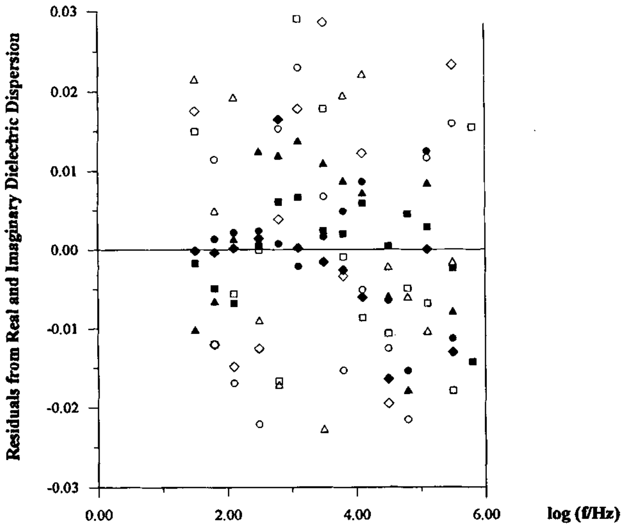

Fig. 6. A plot of the residuals (ε', ε'') against log frequency is given here for PEPP copolymers with chlorine contents of 31 (●, ○), 40 (■, □) and 51% (◆, ◇) at 35°C and 55·6% (▲, △) at 55°C.

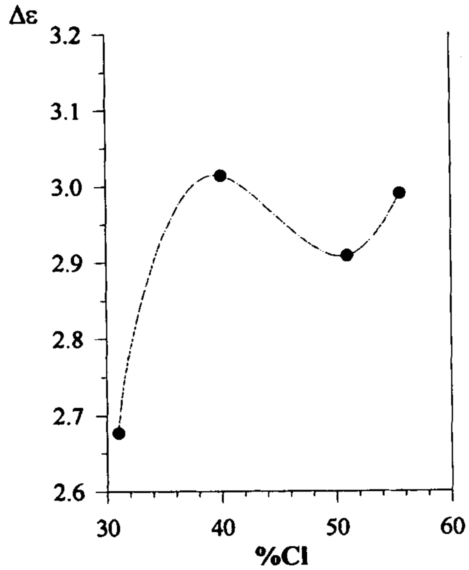

Fig. 7. Variation of the relaxation strength with chlorine content for PEPP copolymers at 35°C with degrees of chlorination of 31, 40, 51 and 55·6%.

TABLE 4. Values of the parameters that define the Kohlrausch–Williams–Watts (KWW) equation

	T (°C)	β	τ_{KWW}
31% Cl	20	0·236	$3{\cdot}082\times10^{-3}$
	25	0·254	$6{\cdot}439\times10^{-4}$
	30	0·259	$1{\cdot}437\times10^{-3}$
	35	0·278	$5{\cdot}166\times10^{-4}$
40% Cl	35	0·254	$5{\cdot}074\times10^{-2}$
	40	0·273	$8{\cdot}059\times10^{-2}$
	45	0·280	$1{\cdot}812\times10^{-3}$
	50	0·300	$4{\cdot}025\times10^{-4}$
51% Cl	25	0·186	$6{\cdot}204\times10^{-2}$
	30	0·197	$9{\cdot}637\times10^{-3}$
	35	0·219	$3{\cdot}980\times10^{-3}$
	40	0·222	$5{\cdot}930\times10^{-4}$
55·6% Cl	50	0·246	$1{\cdot}027\times10^{-2}$
	55	0·270	$2{\cdot}240\times10^{-3}$
	60	0·271	$2{\cdot}061\times10^{-4}$
	65	0·294	$1{\cdot}386\times10^{-4}$

complex dielectric plot (α is a parameter characterizing a symmetrical broadening of the distribution of relaxation times and γ characterizes an asymmetrical broadening).

The values of HN parameters at different temperatures for the chlorinated PEPP studied were calculated by using the Complex Non-linear Least Squares Immitance Fitting Program, LEVM6, written by Ross McDonald.[10] The equivalent electric circuit (a parallel configuration involving a condenser and an HN type impedance, $Z_{\mathrm{HN}} = [1 + (i\omega\tau_0)^{\alpha}]^{\gamma}/i\omega[C_0 - C_{\infty}]$) employed in order to fit the empirical data to the model, is depicted in Fig. 4. The values for PEPP copolymer with 64·3% chlorine have been obtained using the strategy proposed in a previous paper[11] to split the conductivity and interfacial phenomena. The best set of parameters obtained for different chlorinated PEPP samples at different temperatures is given in Table 3, and the accuracy of the fit of HN parameters may be seen in Figs 5 and 6.

In Fig. 7 are presented values of the relaxation strength ($\Delta\varepsilon$) as a function of the chlorine content of PEPP copolymers at 35°C. The values of $\Delta\varepsilon$ at this temperature for copolymers with 55·6% degree of chlorination were obtained assuming a linear variation of this parameter with temperature.[12] The variation of the value of the relaxed dielectric permittivity of the relaxation process (ε_0) with chlorine content (Table 3) is similar to that observed for $\Delta\varepsilon$, that is, a progressive increase until 40% chlorine content, a decrease between 40 and 51%, followed by an increase. The variation of the parameter α is in an inverse sense to that observed for ε_0.

Macroscopic correlation function

According to the phenomenological theory of linear dielectric relaxation, the complex permittivity is related to the normalized decay function $\phi(t)$ by the expression:[13]

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \frac{-\mathrm{d}\phi(t)}{\mathrm{d}t}\,\mathrm{e}^{-i\omega t}\,\mathrm{d}t \tag{3}$$

where $\phi(t)$ is commonly expressed by Kohlrausch–Williams–Watts (KWW) equation:[14,15]

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau_{\mathrm{KWW}}}\right)^{\beta}\right] \tag{4}$$

with β in the range $0 < \beta < 1$. The physical basis of the KWW equation was recently discussed by Ngai and coworkers.[16,17] The model developed by these authors gives for $\phi(t)$ an expression similar to the KWW equation:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau^*}\right)^{(1-n)}\right] \tag{5}$$

where τ^* represents the effective relaxation time, and the parameter n $(0 < n < 1)$ is related to the coupling between the relaxing species; its value is higher the larger the coupling.

From the values of the components of ε^* obtained by means of the HN equation and using methods described elsewhere,[18] the dipolar correlation function $\phi(t)$ was obtained. The values of the β and τ_{KWW} parameters for PEPP copolymers with higher chlorine content at different temperatures are given in Table 4. It can be seen that the β parameter at one specific temperature decreases when the chlorine content increases, suggesting that the interaction between chlorine units that takes place in the dielectric glass–rubber process is higher when the number of these units in the PEPP copolymer increases. This parameter increases with temperature, for all the PEPP copolymers.

CONCLUSIONS

Dielectric relaxation measurements for a set of eight chlorinated polyethylene–polypropylene copolymers reveal that the position of the α peak changes upon introduction of the chlorine units. In contrast with the results of Hößelbarth,[2] we observed an increase in position of the α peak with degree of chlorination up to a value of 40%, a decrease up to 51% and finally a further increase with the chlorine content. This variation of the position of the α peak can be related to the increase in rigidity of the chain caused by inserting chlorine groups. However, because of the large number of possible locations of the chlorine groups and their relative position, a clear explanation of the tendency observed cannot yet be made.

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