

Document downloaded from:

<http://hdl.handle.net/10251/100593>

This paper must be cited as:



The final publication is available at

[https://doi.org/10.1002/\(SICI\)1097-0126\(199611\)41:3<337::AID-PI625>3.0.CO;2-8](https://doi.org/10.1002/(SICI)1097-0126(199611)41:3<337::AID-PI625>3.0.CO;2-8)

Copyright John Wiley & Sons

Additional Information

Dielectric Relaxation in Chlorinated Polyethylene-Polypropylene Copolymers*

Maria Jesús Sanchis, Enrique Sánchez Martínez, Ricardo Díaz Calleja[#]

Departamento de Termodinámica Aplicada, E.T.S.I.I. Universidad Politécnica de Valencia, Apto. 22012, 46071 Valencia, Spain.

Eugenia T. Pankratova, Igor Murin

Department of Chemistry, St. Petersburg State University, Universitetskaya nab. 7/9, 199164 St. Petersburg, Russia

Abstract: Dielectric relaxation measurements were carried out in eight chlorinated polyethylene-polypropylene copolymers (PEPP) 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 T_g -temperature towards higher values, excepting in the range between 40-51% chlorine where an anomalous behaviour was observed. The same tendency is also observed in the strength of the relaxation ($\Delta\epsilon$). The value $\Delta\epsilon$ has been evaluated by using a non linear squares regression program (LEVM6) to calculate the parameters of Havriliak-Negami empirical equation. It does appear reasonable to assume that the anomalous observed behaviour 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.

* The authors wish to dedicate this paper to Professor Günter Klar on the occasion of his sixtieth Birthday.

INTRODUCTION

It is well known that the substitution of chlorine atoms in polyolefines and polyvinylchloride leads to a considerable change of physical properties^{1, 2}, and also, that the dielectric activity of non polar polymers is increased via decoration with polar groups. For example, the polyethylene (PE) is rendered dielectrically active by introducing carbonyl ($>C=O$) and chlorine ($-Cl$) groups in the chain.^{3, 4}

In the present work, we have studied the effect of the addition of chlorine atoms on the dielectric properties for a set of eight chlorinated polyethylene-polypropylene copolymers (PEPP) and we tried to correlate several characteristic parameters (T_g , relaxation intensity, position of dielectric loss peak,...) with the chlorine content.

This system allows us the study of the change of dynamic dielectric properties with increasing the amount of chlorine in the polymer chains. Although, it can be expected that chlorination of PEPP changes gradually the dielectric properties with the of chlorine content, it is possible that at certain content of chlorine atoms, dipole-dipole interactions became important and consequently the dielectric properties could reflect this fact.

For example, it is well known, that the α peak relaxation can be correlated with the glass transition temperature (T_g), and this parameter varies widely with structure and other parameters (intermolecular forces, intrachain steric hindrance, symmetrical substitution, bulky stiff side groups,...). But the most important factor affecting the glass transition temperature is the 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 stiff the chain clearly cause a large increase in T_g , and 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 will restrict rotation. According to this concept, with increasing degree of chlorination of PEPP copolymers, the glass temperature would rise, since the chains would be expected to become less flexible, and the cohesive forces between the chains become even stronger when the number of dipoles (Cl atoms) on the polymer chains increase. Recently, Höbelbarth² has studied, by DSC measurements, the variation of the glass temperature T_g with increasing chlorine content for chlorinated polyethylene (PE-C) and chlorinated polyvinylchlorid (PVC-C),

and he has found a continuous rise of the T_g with the degree of chlorination in both cases.

EXPERIMENTAL

Preparation of polymers

The eight chlorinated ethylene and propylene copolymers studied, were synthesized at 293K in the presence oligoazine of diacetyl without light irradiation. The degree of chlorination (% chlorine in 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 paper⁵.

Dielectric measurements

Dielectric relaxation measurements by the conventional *a.c.* technique were carried out with a DEA 2970 equipment from TA Instruments at twenty frequencies over the range 10^{-1} and 10^5 Hz. The samples were moulded on disc-shaped pill of 1 mm thickness. The temperature ranges in each case where selected in order to capture the glass-rubber relaxation region. The frequency scans were taken at a heating rate of $1^\circ\text{C}\cdot\text{min}^{-1}$.

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 Figure 1. We can see in this plot that the position in the temperature axis of the loss peak shifts progressively to higher temperatures except in the range between 40-51% chlorine content where it is observed that the peak corresponding to the α relaxation passes through a maximum for 40% of chlorine, decrease until the chlorine content is 51% and then increase again.

As an example, the imaginary part of the dielectric permittivity as a function of the temperature at different frequencies and as a function of the frequency at different temperatures (in the range where α relaxation is presented) for one of the PEPP copolymers studied can be seen in Figure 2.

In order to have a better understanding of the observed behaviour for the variation of the temperature of the maximum of the loss peak (ϵ'') with the degree of chlorination of PEPP, we represent in figure 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 PVC and PVDC taking from bibliography⁶.

To explain the above peculiar behaviour, we have compared the experimental data of α relaxation peak observed for each one of chlorinated PEPP copolymers with that one assigned to other related polymers^{2, 6}. Thus, in spite of the increase in chlorine groups, the T_g for the polyvinylidene chloride (PVDC), 254.9K, is about 98K lower than the value of 353.6K for the polyvinyl chloride (PVC). According to Wüerstlin⁷ this difference 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 the case of the non-polar polyisobutylene (PIB, 202K) or with other polar polymers as the polyvinylidene fluoride (PVDF, 238K), polyvinyl fluoride (PVF, ~303K) and polyvinyl bromide (PVBr, 373K) suggest that the steric factors may be largely involved. So, the temperature of the glass transition is about 50K lower for PVF than the 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 corresponding to chlorine. Differences in polarity seem unlikely to be involved to a large extent, as evidenced by the fact that the dipole moment of CH₃Cl (1.87 D) is only slightly larger than that of CH₃F (1.81D). According to it the anomalous behaviour observed could be related to a steric repulsion between groups more voluminous in alternate chain atoms, which is thought to lead to a distortion of main-chain valences angles.

Modelling of the relaxation peaks

It is interesting to fit the empirical data to some empirical model in order to get information from the characteristics parameters of these empirical model. Therefore, in our case the peaks are fitted by an empirical equation of the type⁸

$$\epsilon'' = \epsilon''_{max} \cdot \operatorname{sech} mx \quad (1)$$

with $x = \frac{f}{f_{max}}$, 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 intramolecular interaction among the relaxing species in such a way that the larger is the parameter (the unity is its maximum value), the lower are the interactions. The results summarized in Table 2 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 of the volume in the polymer.

In order to quantify more closely the dielectric relaxation processes we represent them in terms of Cole Cole plot, 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 the dielectric relaxation are skewed arcs. The curves are customarily fitted by the Havriliak-Negami (HN) empirical equation⁹

$$\epsilon^* = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{[1 + (i\omega\tau_0)^{\alpha}]^{\gamma}} \quad (2)$$

where ϵ_0 and ϵ_{∞} are the relaxed and unrelaxed dielectric permittivity of the relaxation process, $\Delta\epsilon$ is the relaxation strength, τ_0 is the central relaxation time, ω is the angular frequency and α , γ are parameters related with the shape and skewness of 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 Nonlinear Least Squares Impedance Fitting Program LEVM6 written by Ross McDonald¹⁰. The equivalent electric circuit (a parallel configuration involving a condenser, and a Havriliak-Negami type impedance, $Z_{HN} = [1 + (i\omega\tau_0)^{\alpha}]^{\gamma} / i\omega[C_0 - C_{\infty}]$) employed in order to fit the experimental data to the model is depicted in Figure 4. The values for PEPP copolymer with a 64.3% of chlorine have been obtained using the strategy proposed in a previous paper¹¹ 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 figure 5 and 6.

In figure 7 are represented the values of the strength relaxation ($\Delta\epsilon$) as a function of the chlorine content of the PEPP copolymers at 35°C. The values of $\Delta\epsilon$ at this temperature for copolymers with 55.6% degree of chlorination were obtained assuming a linear variation of this parameter with the temperature¹². The tendency of the value of the relaxed dielectric permittivity of the relaxation process (ϵ_0) with the chlorine content (Table 3) are similar to that one observed for $\Delta\epsilon$, that is, a progressive increase until 40% chlorine content, a decrease between 40-51% and again an increase and the variation of the parameter α is in inverse sense with that one 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 expression¹³

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \frac{-d\phi(t)}{dt} e^{-i\omega t} dt \quad (3)$$

where $\phi(t)$ is commonly expressed by the Kohlrausch-Williams-Watts (KWW) equation^{14, 15}

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

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

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

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

From the values of the components of ϵ^* obtained by means of the HN equation and using methods described elsewhere¹⁸, 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 take place in the dielectric glass-rubber process is higher when the number of these units in PEPP copolymer increases; and this parameter increase with temperature, for every 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 Höβelbarth² we observe at the increasing position of the α -peak with the degree of chlorination until a degree of chlorination of 40%, a decreasing until 51% and finally the position of the α -peak increases with the chlorine content. The tendency of the increase of the position the of α -peak can be related with the increase of rigidity of the chain by inserting chlorine groups. However, because of the high number of possible locations of the chlorine groups and their also high number possible relative position of them, a clear explanation of the tendency observed are not yet fully understood.

REFERENCES

- 1 Petersen, J., Ranby, B., *Makromol. Chem.*, **102** (1967) 83, **133** (1970) 263
- 2 Hößelbarth, B., *Angew.Makromol. Chem.*, **231** (1995) 161
- 3 Ashcraft, C.R., Boyd, R.H., *J.Polymer Science*, **14** (1976) 2153
- 4 Matsuoka, S., Roe, R.J., Cole, H.F., *A comparative study of dielectric behaviour of polyethylene and chlorinated polyethylene* in "Dielectric Properties of Polymers" F. Karasz, Ed. Wiley 1972
- 5 Pankratova, E.T., Lubnin, A.B., *Vysokomol.Soed.* **28B** (1986) N12 912
- 6 McCrum, N.G., Read, B.E., Williams, G., "Anelastic and Dielectric Effects in Polymeric Solids", Ed. Dover 1991
- 7 Würstlin, F. *Kolloid Z.*, **120** (1951) 84
- 8 Fuoss, R.M., Kirkwood, J.G., *J. Am. Chem. Soc.* **63** (1941) 385
- 9 Havriliak, H., Negami, S., *J. Polymer Scien. Part. C*, **11** (1966) 99
- 10 Ross Macdonald, J., "Impedance Spectroscopy", Ed. Willey, 1987
- 11 Sanchis, M. J., Díaz Calleja, R., Gargallo, L., Radic', D., *Macromol. Rapid Commun.* **15** (1994) 31
- 12 Buerger, D.E., Boyd, R.H., *Macromolecules* **22** (1989) 2694
- 13 Williams, G., Watts, D.C., Dev, S.B., North, A.M., *Trans. Fadaray Soc.*, **67** (1971) 1323
- 14 Kohlrausch, R., *Prog. Ann. Phys.*, **12(3)** (1947) 3931
- 15 Williams, G., Watts, D.C., *Trans. Fadaray Soc.*, **66** (1970) 80
- 16 Ngai, K.L., Rajagopal, A.K., Teitler, S.J., *J. Chem.Phys.*, **88** (1988) 5086
- 17 Ngai, K.L., Mashimo, S., Fytas, G., *Macromolecules*, **21** (1988) 3030
- 18 Nunes, R.C., Díaz-Calleja, R., Pinto, M., Saíz, E., Riande, E., *J. Phys. Chem.*, **99** (1995) 12962

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

	Cl content in mass	W_n (g·mol ⁻¹)	Distribution of Cl-atoms on different groups			
			-CH ₂ Cl	=CHCl	≡CCl	-CHCl ₂
PEPP	0 %	29000	0	0	0	0
PEPP 2.5% Cl	2.5 %	28700	0.09	0.34	0	0
PEPP 4.5% Cl	4.5 %	29300	0.17	0.62	0.1	0
PEPP 6.5% Cl	6.5 %	28000	0.24	0.90	0.25	0
PEPP 31% Cl	31 %	29400	1.16	6.20	1.40	0
PEPP 40% Cl	40 %	28600	1.50	9.1	2.80	0.20
PEPP 51% Cl	51 %	27800	2.70	12.3	2.80	0.20
PEPP 55.6% Cl	55.6 %	29300	2.9	13.7	2.80	0.20
PEPP 64.3% Cl	64.3 %	28500	3.3	13.7	2.80	1.30

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

Table 3. Havriliak-Negami Parameters ($\Delta\epsilon$, ϵ_∞ , α , γ , τ) for PEPP copolymers studied at different temperatures.

	T (°C)	ϵ_∞	ϵ_0	$\Delta\epsilon$	τ	α	γ
PEPP 2.5% CI	-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% CI	-45	2.028	2.322	0.294	$2.9520 \cdot 10^{-2}$	0.302	0.745
	-40	2.000	2.325	0.325	$4.3566 \cdot 10^{-3}$	0.291	0.746
	-35	1.9532	2.3262	0.373	$5.5771 \cdot 10^{-4}$	0.284	0.757
	-30	1.943	2.319	0.376	$1.7145 \cdot 10^{-4}$	0.288	0.762
PEPP 6.5% CI	-40	2.191	2.740	0.627	$1.9838 \cdot 10^{-3}$	0.326	0.546
	-35	2.190	2.821	0.631	$4.0034 \cdot 10^{-4}$	0.326	0.625
	-30	2.216	2.814	0.598	$1.0206 \cdot 10^{-4}$	0.337	0.708
PEPP 31% CI	20	2.622	5.547	2.925	$6.2134 \cdot 10^{-3}$	0.402	0.600
	25	2.618	5.425	2.807	$1.1206 \cdot 10^{-3}$	0.419	0.630
	30	2.603	5.295	2.692	$4.2872 \cdot 10^{-3}$	0.480	0.540
	35	2.592	5.269	2.677	$1.3323 \cdot 10^{-3}$	0.490	0.560
PEPP 40% CI	35	2.711	5.724	3.014	$3.7631 \cdot 10^{-2}$	0.380	0.800
	40	2.717	5.617	2.900	$6.5175 \cdot 10^{-2}$	0.410	0.795
	45	2.728	5.588	2.860	$2.0123 \cdot 10^{-3}$	0.440	0.730
	50	2.722	5.520	2.798	$8.6870 \cdot 10^{-4}$	0.510	0.590
PEPP 51% CI	25	2.475	5.401	2.926	$4.9530 \cdot 10^{-1}$	0.393	0.436
	30	2.453	5.372	2.919	$6.4639 \cdot 10^{-2}$	0.406	0.449
	35	2.432	5.340	2.908	$1.1906 \cdot 10^{-2}$	0.416	0.473
	40	2.414	5.311	2.896	$2.4816 \cdot 10^{-3}$	0.421	0.499
PEPP 55.6% CI	50	2.616	5.204	2.588	$8.8046 \cdot 10^{-3}$	0.380	0.765
	55	2.647	5.151	2.504	$2.4890 \cdot 10^{-3}$	0.426	0.726
	60	2.651	5.081	2.430	$2.6201 \cdot 10^{-4}$	0.440	0.700
	65	2.653	5.022	2.369	$2.5660 \cdot 10^{-4}$	0.490	0.626
PEPP 64.3% CI	100	2.295	4.097	1.798	$8.84412 \cdot 10^{-2}$	0.614	0.219

Table 4. Values of the parameters that define the Kohlrauch-Williams-Watts (KWW) equation.

	T (°C)	β	τ_{kww}
31% CI	20	0.236	$3.082 \cdot 10^{-3}$
	25	0.254	$6.439 \cdot 10^{-4}$
	30	0.259	$1.437 \cdot 10^{-3}$
	35	0.278	$5.166 \cdot 10^{-4}$
40% CI	35	0.254	$5.074 \cdot 10^{-2}$
	40	0.273	$8.059 \cdot 10^{-2}$
	45	0.280	$1.812 \cdot 10^{-3}$
	50	0.300	$4.025 \cdot 10^{-4}$
51% CI	25	0.186	$6.204 \cdot 10^{-2}$
	30	0.197	$9.637 \cdot 10^{-3}$
	35	0.219	$3.980 \cdot 10^{-3}$
	40	0.222	$5.930 \cdot 10^{-4}$
55.6% CI	50	0.246	$1.027 \cdot 10^{-2}$
	55	0.270	$2.240 \cdot 10^{-3}$
	60	0.271	$2.061 \cdot 10^{-4}$
	65	0.294	$1.386 \cdot 10^{-4}$

Figure captions

Figure 1. Temperature dependence of the dielectric loss ϵ'' for eight chlorinated PEPP copolymers studied at 100 Hz (■ 2.5%, ● 4.5%, △ 6.5%)

Figure 2. Variation of the dielectric loss ϵ'' with (a) the 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) the 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%.

Figure 3. Variation of the temperature of the maximum of the loss peak (ϵ'') with the chlorine content for PEPP copolymers with 31, 40, 51, 55.6% Cl and other related polymers, △ PVC, □ PVDC.

Figure 4. Electrical circuit representing the dielectric process.

Figure 5. Complex plane representation of PEPP copolymers with a chlorine content of 31,40 and 51% at 35°C and 55.6% at 55°C.

Figure 6. A plot of the residuals (ϵ' , ϵ'') against log frequency is given here for PEPP copolymer with a chlorine content of 31 (●,○), 40 (■, □) and 51% (◆, ◇) at 35°C and 55.6% (△, Δ) at 55°C.

Figure 7. Variation of the strength of the relaxation with the chlorine content for PEPP copolymers at 35°C with at degree of chlorination of 31, 40, 51, 55.6% .

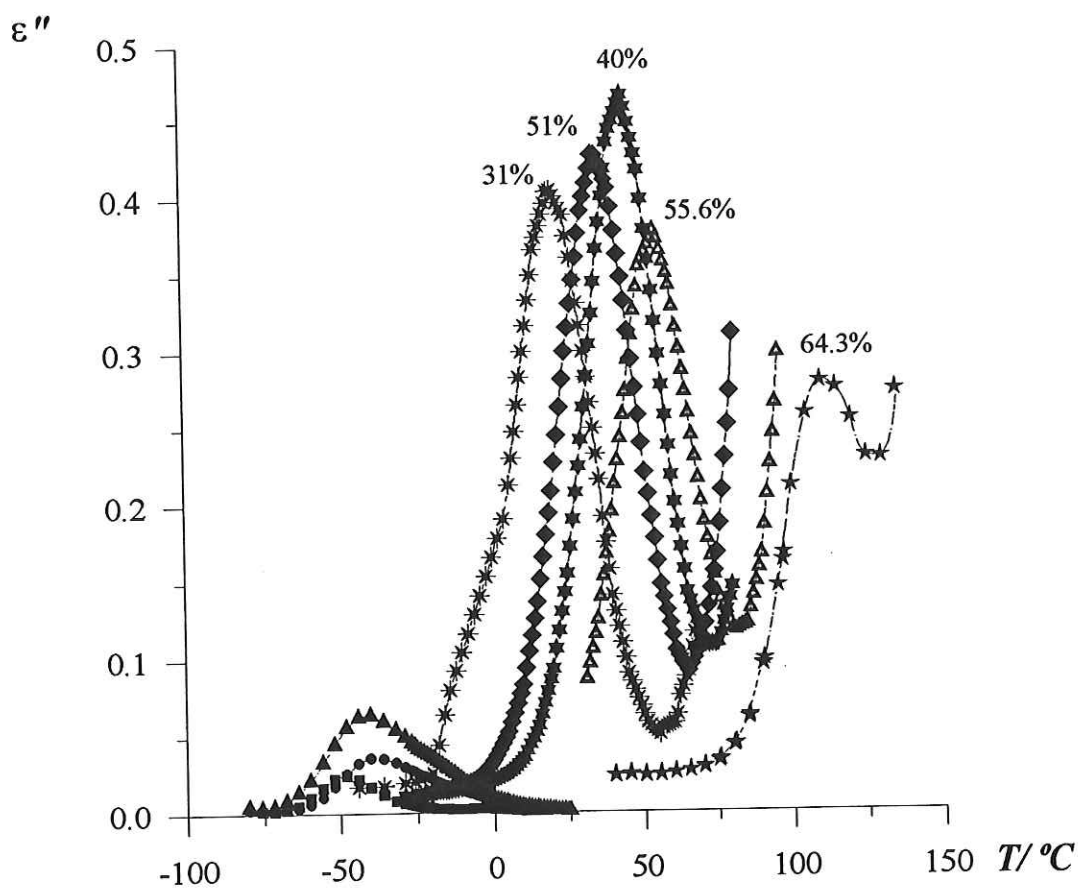
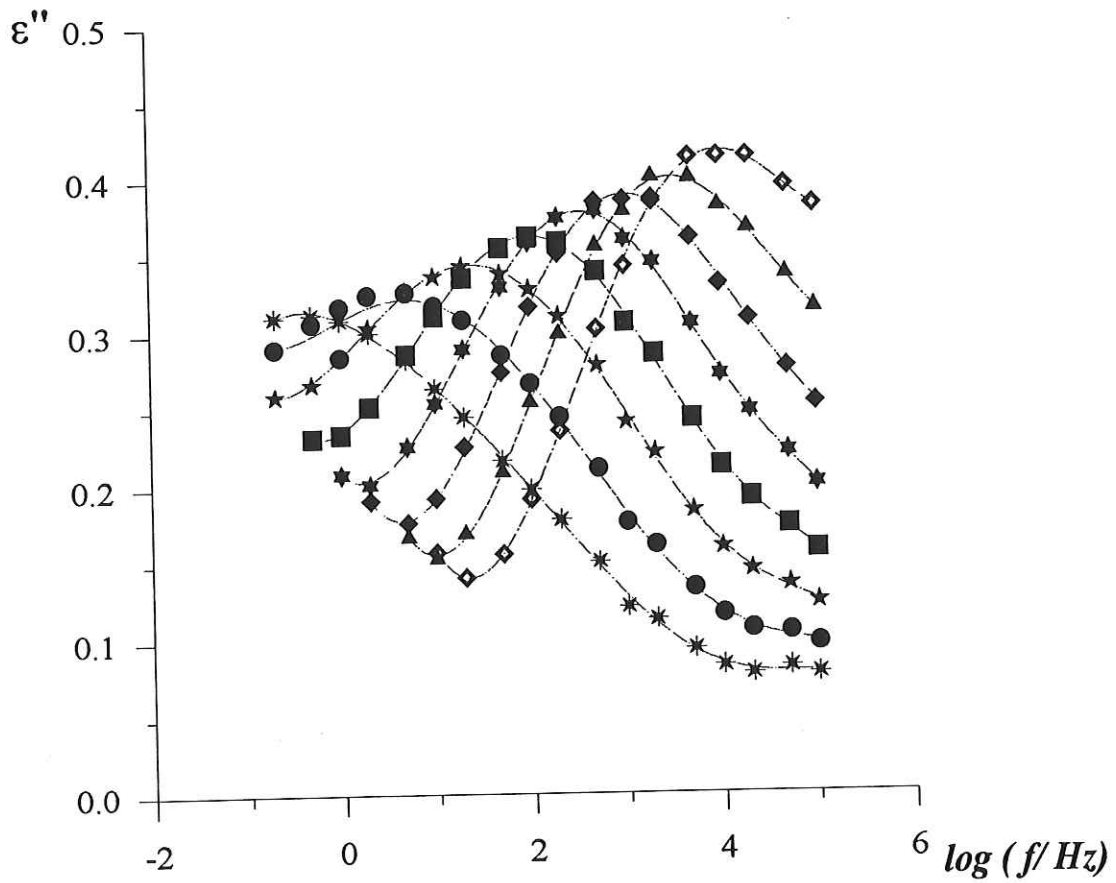
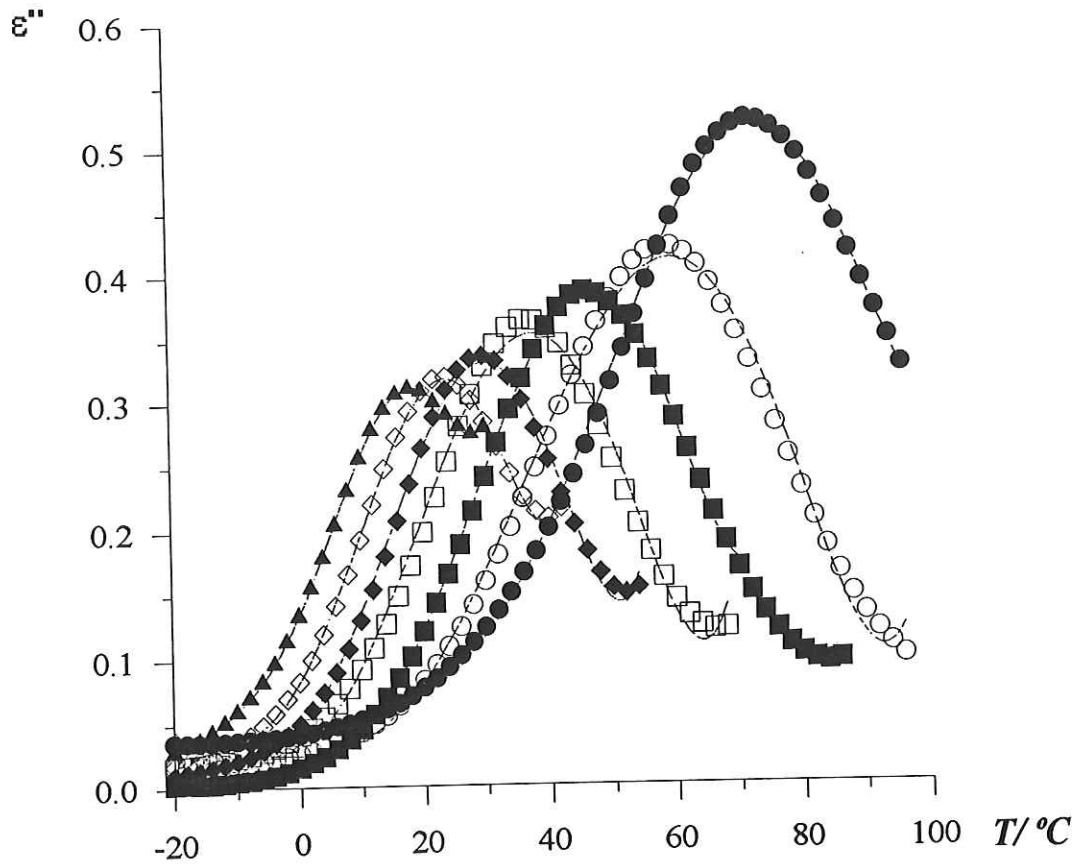


Figure 1
 Maria Jesús Sanchis, Enrique Sánchez,
 Ricardo Díaz-Calleja, Eugenia T.
 Pankratova, Igor Murin
 "Dielectric Relaxation in Chlorinated-...
 Polypropylene Copolymers"



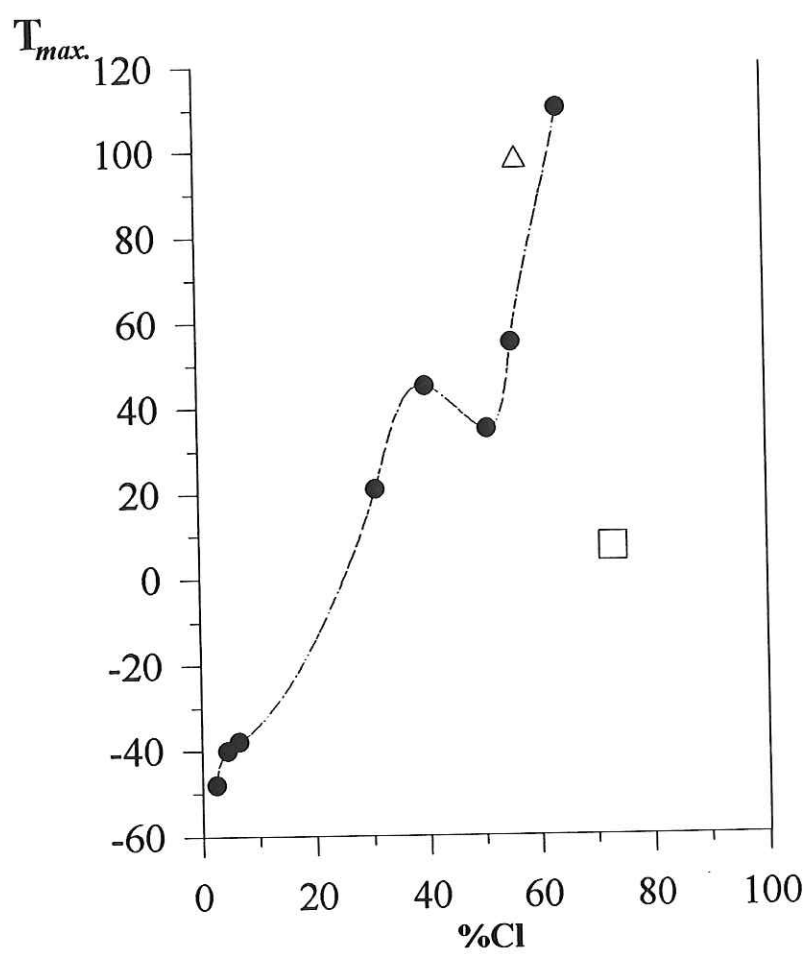


Figure 3
 Maria Jesús Sanchis, Enrique Sánchez,
 Ricardo Díaz-Calleja, Eugenia T.
 Pankratova, Igor Murin
 "Dielectric Relaxation in Chlorinated-....
 Polypropylene Copolymers"

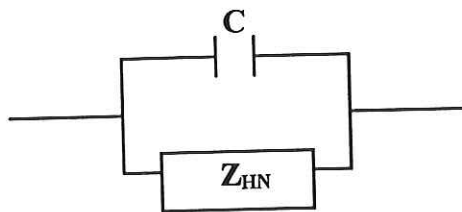


Figure 4
*Maria Jesús Sanchis, Enrique Sánchez,
Ricardo Díaz-Calleja, Eugenia T.
Pankratova, Igor Murin*
“Dielectric Relaxation in Chlorinated...
Polypropylene Copolymers”

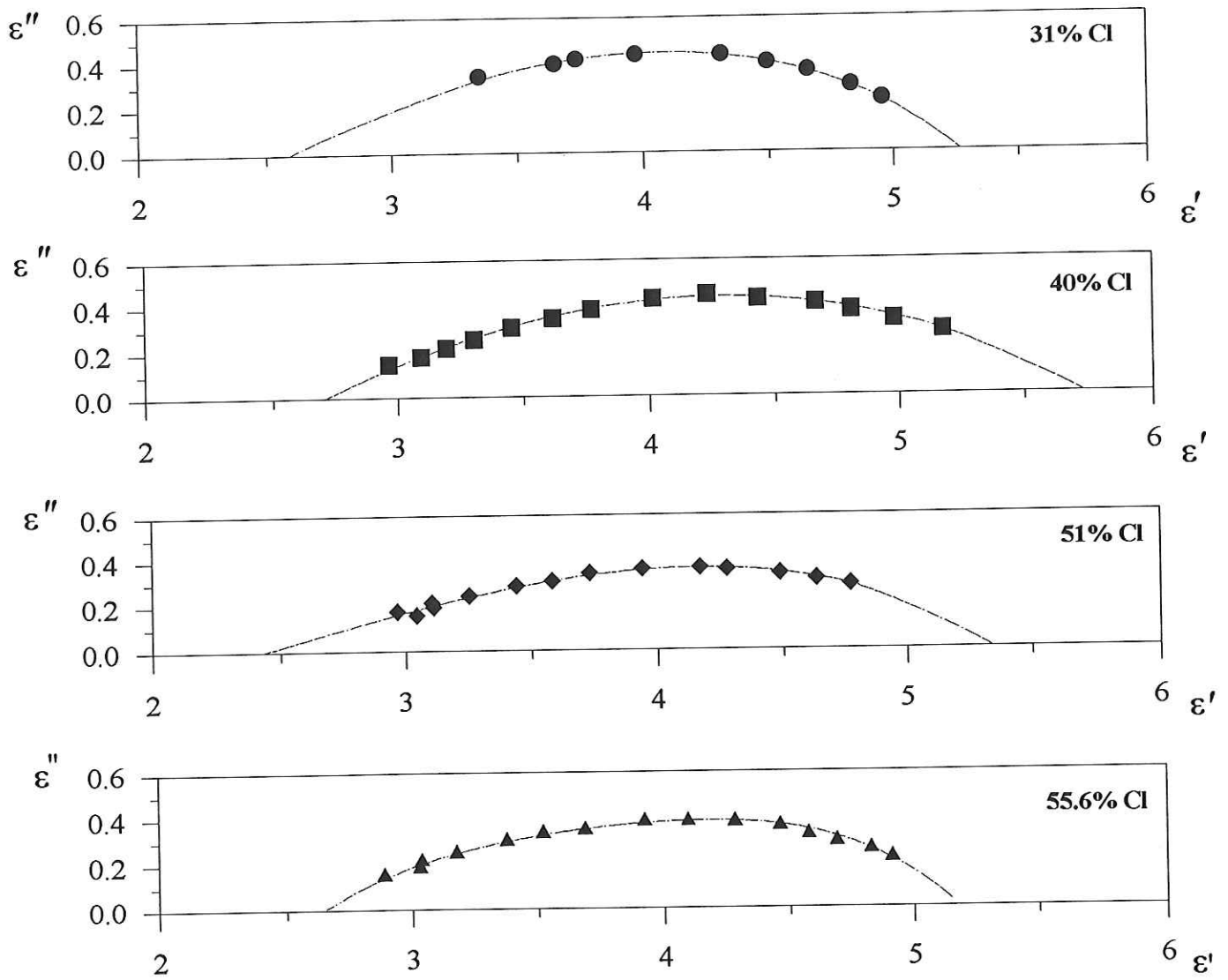


Figure 5
 Maria Jesús Sanchis, Enrique Sánchez,
 Ricardo Díaz-Calleja, Eugenia T.
 Pankratova, Igor Murin
 "Dielectric Relaxation in Chlorinated-...
 Polypropylene Copolymers"

Residuals from Real and Imaginary Dielectric Dispersion

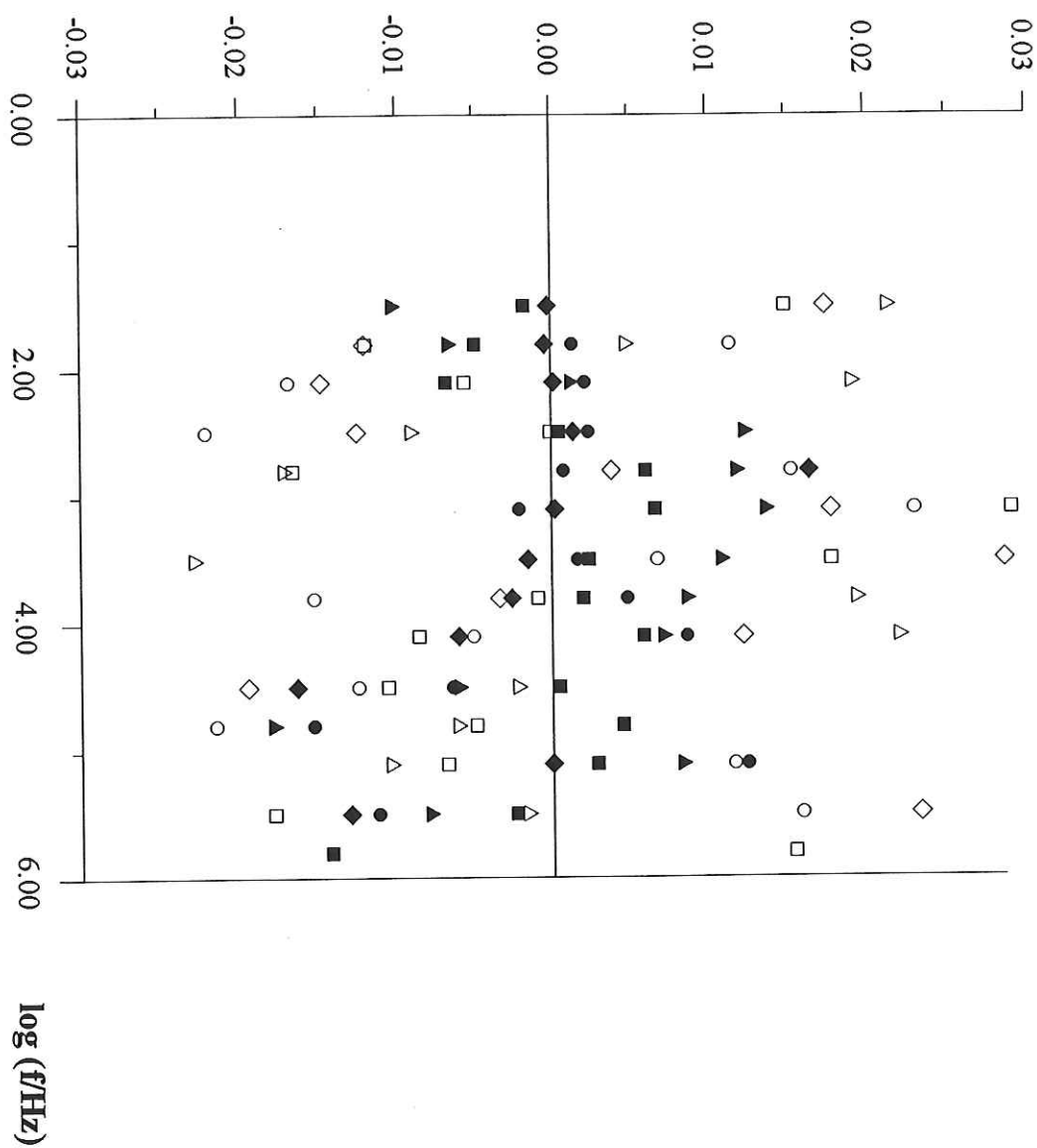


Figure 6

*Maria Jesús Sanchis, Enrique Sánchez,
Ricardo Díaz-Calleja, Eugenia T.
Pankratova, Igor Murin*
"Dielectric Relaxation in Chlorinated-
Polypropylene Copolymers"

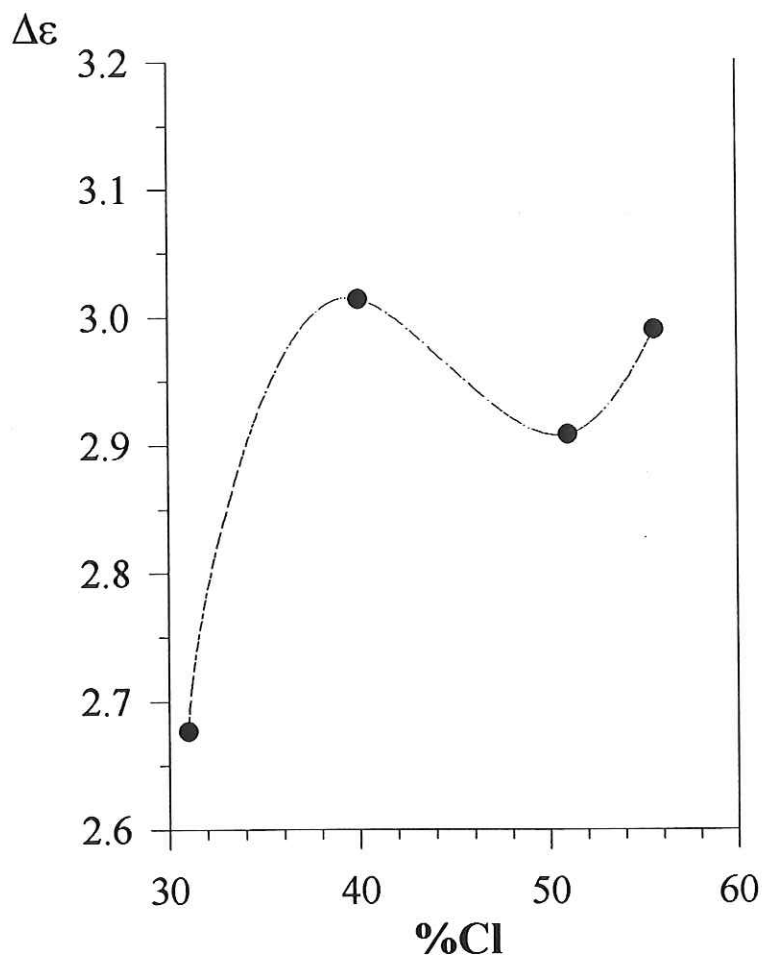


Figure 7
*Maria Jesús Sanchis, Enrique Sánchez,
Ricardo Díaz-Calleja, Eugenia T.
Pankratova, Igor Murin*
"Dielectric Relaxation in Chlorinated-...
Polypropylene Copolymers"