Dielectric Spectroscopy Analysis of Recycled PET with Different Synthetic Polymer Blends

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Abstract-: Focused on broadband dielectric analysis of recycled PET with different synthetic polymer blends via broadband dielectric spectroscopy, the article tries to emphasize different aspects of polarization and the charge transport in the material, by an alternative representation of dielectric properties.

I. Introduction

The complex dielectric function ε*(ω) in its dependence on angular frequency ω = 2πν (ν – frequency of the outer electrical field) and temperature originates from different processes: (i) microscopic fluctuation of molecular dipoles, (ii) the propagations of mobile charges carriers (translation diffusions of electrons, holes or ions), and (iii) the separation of charges at the interface which gives rise to an additional polarization. The latter can take place at inner dielectric boundary layers (Maxwell/Wagner/Sillars-polarization [2, 3]) on a mesoscopic scale and/or at the external electrodes contacting the sample (electrode polarization) on a macroscopic scale. Its contributions to the dielectric loss can be orders of magnitude larger that the dielectric response due to molecular fluctuations.

Each of the above mentioned processes has specific features in the frequency and temperature dependence of the real part of the complex dielectric function. It is the objective of this paper to discuss the method, to analyze, to separate and to quantify their different contributions to the dielectric spectra.

The relaxation processes are characterized by a peak in the imaginary part ε' of the complex dielectric function ε*(ω) = ε'(ω)-iε''(ω) (i = $\sqrt{-1}$) with increasing frequency. In contrast, conduction phenomena show an increase of the imaginary part of the dielectric function with decreasing frequency. For pure ohmic conduction the real part of ε*(ω) is independent of frequency while for non-ohmic conduction or polarization effects (at inner boundaries or external electrode) the real part of ε*(ω) increases with decreasing frequency. A schematic representation of the frequency dependence of is given in figure 1.

Alternative representation of the dielectric properties of materials are the complex conductivity σ*(ω). This emphasize different aspects of polarization and charge transport in a material.

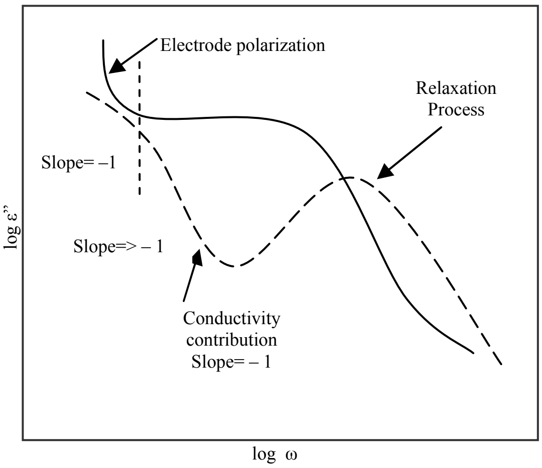


Fig. 1. Scheme of the real ε' (solid line) and the imaginary ε'' (dashed line) part of the complex dielectric function for relaxation process and an ohmic and non-ohmic conductivity

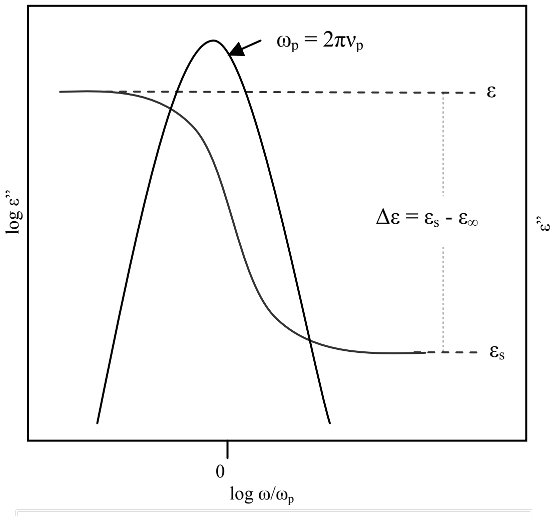


Fig. 2. Real ε' and the imaginary part ε'' of the complex dielectric function vs. normalized frequency for a Debye relaxation process

One of the most important applications of dielectric spectroscopy in investigation of relaxation processes which are due to rotational fluctuation of molecular dipoles. As they are related to characteristic parts of a molecule (functional group) or the molecule as whole, information about the dynamics of a molecular ensemble can be obtained by analyzing the dielectric function. In the frequency $\nu = \omega/2\pi$ of the applied outer dielectric field corresponds to reorientation times τ of molecular dipoles the complex dielectric function shows a characteristic pattern. With increasing ω the real part $\varepsilon'(\omega)$ decreases step like whereas the imaginary mart exhibits a maximum. The essential quantities which characterize a dielectric relaxation process can be extracted from behavior. The frequency of maximal loss ν_p is related to characteristic relaxation rate $\omega = 2\pi\nu_p$ or relaxation time $\tau_p = 1/\omega_p$ of the fluctuating dipoles. From the shape of the loss peak the distribution of relaxation times can be deduced. The dielectric strength $\Delta\varepsilon$ of the relaxation process can be determined either from the area under the loss peak $\varepsilon''(\omega)$or from the step in $\varepsilon'(\omega)$.

II. Experimental Part

Dielectric relaxation processes are usually analyzed using model functions. Starting from the theoretically well founded Debye function several formulas for both the frequency and the time domain have been suggested to describe the experimentally observed spectra. The most important of these approaches are discussed below.

The Debye function for frequency dependence of $\varepsilon^*(\omega)$ is given by:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \Delta\varepsilon(1 + \mathrm{i}\cdot\omega\cdot\tau_D) \qquad (1)$$

where $\Delta\varepsilon = \varepsilon_S - \varepsilon_\infty$ is the dielectric relaxation strength or intensity with $\varepsilon_S = \lim_{\omega\tau<<1} \varepsilon'(\omega)$ and $\varepsilon_\infty = \lim_{\omega\tau>>1} \varepsilon'(\omega)$. The Debye relaxation time τ_D is related to the position of maximal loss by $\omega_p = 2\omega\nu_p = 1/\tau_D$ (see figure 2). The loss peak is symmetric with a half width ω_D of 1.14 decades.

In most cases the half width of measured loss peaks is much broader than predicted by equation 1 (up to six decades) and in addition their shapes are asymmetric with a high frequency tail. This is called non-Debye (or non ideal) relaxation behavior. In the literature several empirical model functions – mostly generalizations of the Debye function – have been developed and tested which are able to describe broadened and/or asymmetric loss peaks.

A broadening of the dielectric function can be described by the Cole/Cole-function

$$\varepsilon^*_{CC} = \varepsilon_\infty + \Delta\varepsilon/(1 + (\mathrm{i}\cdot\omega\cdot\tau_{CC})^\beta) \qquad (2)$$

where $0<\beta\leq1$ leads to a symmetrical broadening for the relaxation function compared to equation 1. For $\beta=1$ the Debye-function is obtained. The Cole/Cole-relaxation time τ_{CC} gives the position of maximal loss by $\omega_p = 2\omega\nu_p = 1/\tau_{CC}$.

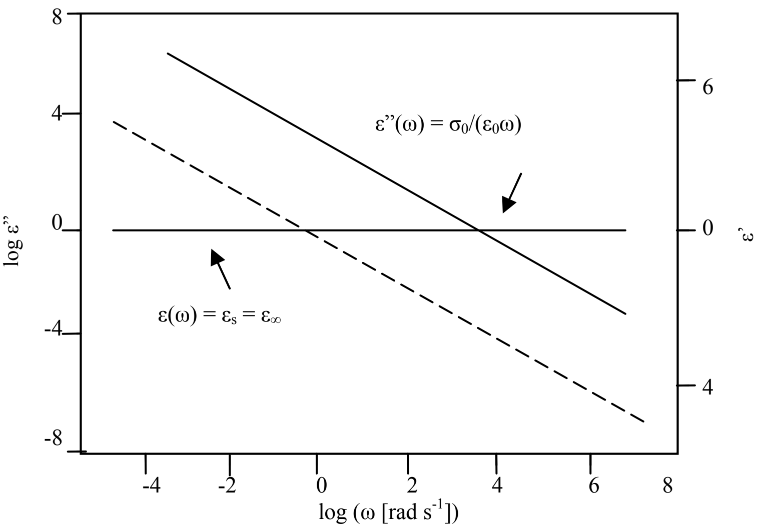


Fig. 3. Theoretical example for complex dielectric function whit pure ohmic contribution: $\sigma_0/\varepsilon_0 = 1$(dashed line), $\sigma_0/\varepsilon_0 = 10^4$ (solid line), $\varepsilon' = 5$

According to Maxwell's equations the current density $j=\sigma^*E$ and the time derivative of the dielectric displacement $dD/dt = i\omega\varepsilon^*\varepsilon_0E$ are equivalent where σ^* is the complex conductivity. Hence for sinusoidal electrical fields $E(\omega) = E_0=e^{j\omega t}$ and $\varepsilon^*(\omega)$ and $\sigma^*(\omega)$ are related to each other by $\sigma^*(\omega) = \sigma'(\omega) + i\sigma^*(\omega) = i\omega\varepsilon'\varepsilon^*(\omega)$ (1). The real and imaginary part of $\sigma^*(\omega)$ is given by $\sigma'(\omega) = i\omega\varepsilon_0\, \varepsilon''(\omega)$; $\sigma''(\omega) = i\omega\varepsilon_0\varepsilon'(\omega)$ (2).

For pure electronic conduction no contribution arises while $\varepsilon'(\omega) = \sigma_0/\varepsilon_0\omega$ increases linearity with decreasing frequency. σ_0 is the (electronic) d.c.- conductivity. Hence in the conductivity representation for electronic conduction the real part $\sigma'(\omega)$ is constant (σ_0) and the imaginary part σ'' increases linearly with frequency.

It is remarkable that the complex conductivity σ^* is similar in its frequency temperature dependence (including also charge carrier concentration) dependence for a board variety of quite different materials, e.g. ionic gasses, ion conducting polymers, electron conducting conjugated polymers, or electron conducting carbon black composites

III. Results and Discussion

Composites based on the recycled polyethylene terephtalate (RPET) with polyethylene (PE), polypropylene (PP), polycarbonate (PC) and poly(ethylene-co-glycidyl methacrylate (PE-co-GMA) were obtained and properties of the resulting material were evaluated.

The composites were obtaining by mixing the polymers in the same ratio (70:30) at 260°C, by melt-extrusion [4, 5]. Real part ε of permittivity decrease with the increasing of frequency and the maximum values of permittivity are between 3.5 and 4, due the electrical relaxation phenomena. All blends have permittivity lower than that PET. Also the imaginary part ε" decrease with the increasing frequency due to conduction figure 5. At the lower frequencies the relaxation contribution to ε' is superimposed by the electrode polarization effects.

Low amount of polyethylene (15-20%) introduced in blends does not influence the property of blends RPET/PE, after 30% PE it can be observed a decrease of blends permittivity because PE has the values of permittivity (2.3) lower than that of the RPET (4.3), figure 6-7.

In the first place it was observed a increase of dielectric losses (until 10 Hz frequency) due to inhomogeneous nature of the polymer blends, figure 8-9.

In our study, test samples with 15x3.1x3.2 mm active section were submitted to a broadband dielectric analyzer (frequency range from 10^{-2} to 10^{9} Hz), equipped with temperature control system and specialized software towards identifying charge migration and dipole orientation mechanisms, with focus on interfacial effects.

For the real part $\sigma'(\omega)$ on the low frequency side a plateau value is obtained which can be extrapolated to the d.c.-conductivity σ_0 for $\omega \rightarrow 0$. At a critical frequency $\omega_c = 2\pi\nu_c$ the dispersion of σ'sets in. The latter can be determined by smoothing the data and calculating numerically the maximum in $\partial^2\sigma'/\partial\omega^2$

In imaginary part of the complex conductivity decreases with decreasing frequency . The increases at the low frequencies indicates electrode polarization. According to Barton/Nakajiama/Namikawa $\omega_c \sim \sigma_0$ (5) holds. For $\omega > \omega_c$ σ' increases strongly with frequency. This behavior is quite general and is found for variety of semi-conducting systems.

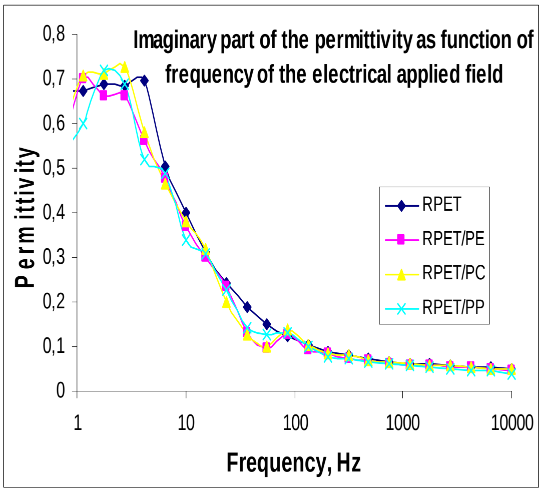


Figure 4. Imaginary part of permittivity vs. electric field applied for RPET, RPET/PE, RPET/PC, RPET/PP

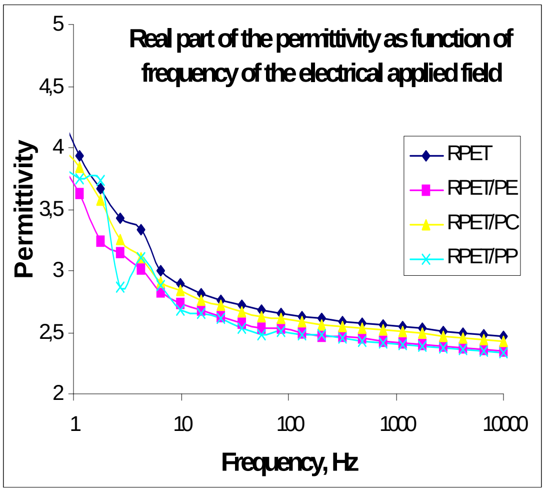
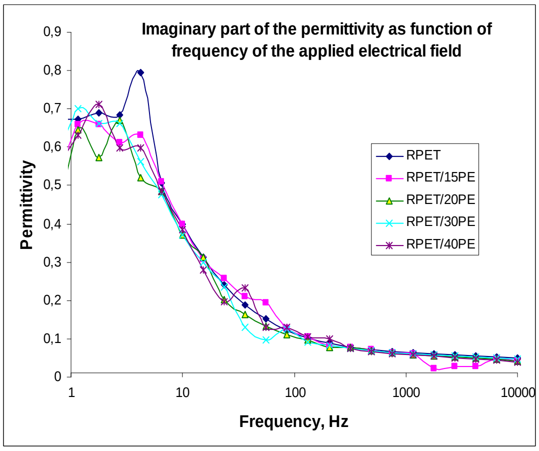


Figure 5. Real part of permittivity vs. electric field applied for RPET, RPET/PE, RPET/PC, RPET/PP



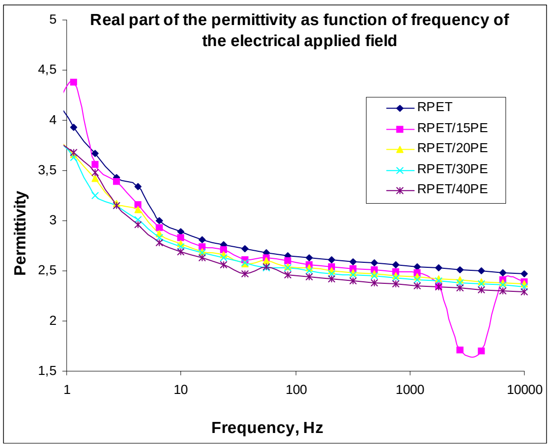
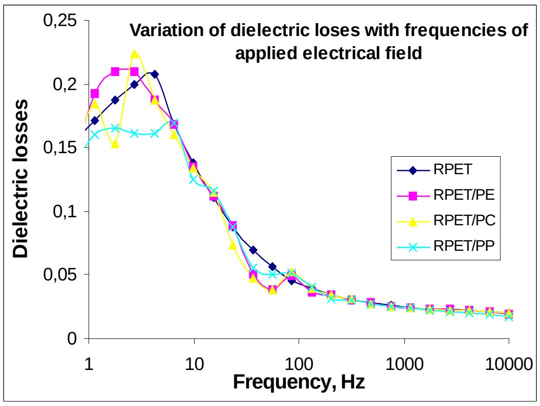


Figure 5. Imaginary part of permittivity vs. electric field applied for RPET, RPET/15PE, RPET/20PE, RPET/30PE, RPET/40PE

Figure 5. Real part of permittivity vs. electric field applied for RPET, RPET/15PE, RPET/20PE, RPET/30PE, RPET/40PE



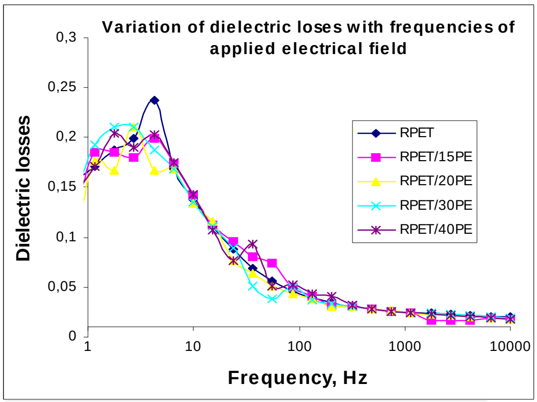
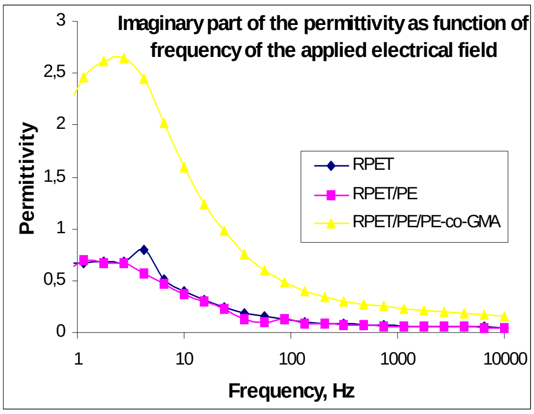


Figure 6. Dielectric loss vs. frequency of electric field applied for RPET, RPET/PE, RPET/PC, RPET/PP

Figure 7. Dielectric loss vs. frequency of electric field applied for RPET, RPET/15PE, RPET/20PE, RPET/30PE, RPET/40PE

The presence of the glycidyl methacrylate groups in compatibilizing agent influences all dielectric properties. Permittivity of blends based on the RPET/PE and compatibilizing agent has bigger values, at low frequency 0.7 Hz the value of the real permittivity is 15.9.



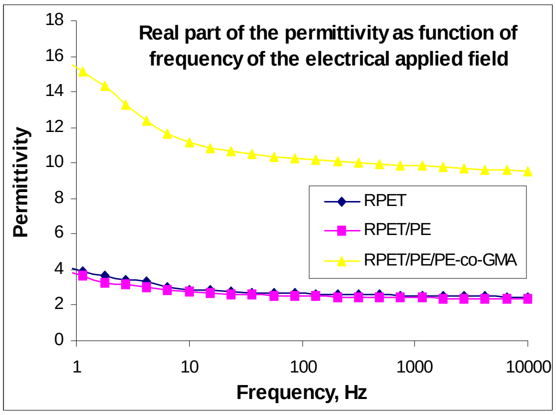


Figure 8. Imaginary part of permittivity vs. frequency of electric field applied for RPET, RPET/PE, RPET/PE/PE co-GMA

Figure 9. Real part of permittivity vs. frequency of electric field applied for RPET, RPET/PE, RPET/PE/PE co-GMA

Compatibilizing agent leads to a increase of dielectric losses due to it structure, which allows electron migration in the amorphous zone.

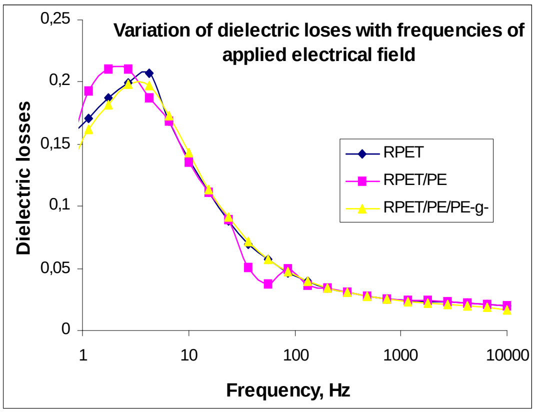


Figure 10. Dielectric loss vs. frequency of electric field applied for RPET, RPET/PE, RPET/PE/PE co-GMA

Samples	RPE %	PE%	PC%	PP%	PE-co-GMA
RPET	100	-	-	-	-
RPET/PE	70	30	-	-	-
RPET/PC	70	-	30	-	-
RPET/PP	70	-	-	30	-
RPET/15E	85	15	-	-	-
RPET/20PE	80	20	-	-	-
RPET/30PE	70	30	-	-	-
RPET/40PE	60	40	-	-	-
RPET/PE/ PE – co-GMA	60	30	-	-	10

Table 1. Composites based on the recycled polyethylene terephtalate (RPET) with polyethylene (PE), polypropylene (PP), polycarbonate (PC) and poly(ethylene-co-glycidyl methacrylate (PE-co-GMA)

In addition to complex permittivity and conductivity figure 3 gives the complex modulus representation for the data above. Model function like KWW or the Cole/Davidson function transformed into the conductivity representation has been used to analyze the frequency dependence of the complex dielectric conductivity modulus. Neither KWW or the Cole/Davidson function can describe in the whole frequency range. Jonscher proposed the following equation: (3)

$$\sigma^{'}(\omega) = \sigma_0 + A\omega^S = \sigma[1 + (\omega\tau)^S]$$

for the frequency dependence of the real part of the complex conductivity. In equation (3) τ is time constant for conductivity relaxation related to ω_c. For $\omega >> 1/\tau$ equation (3) gives a power low characteristic by $(0 < s \leq)$ while for $\omega << 1/\tau$ the d.c. conductivity σ_0 is recovered

IV. Conclusions

The work tried to emphasize some aspects of polarization and charge transport in PE/PET, by an alternative representation of dielectric properties. Accordingly, samples (characterized by molecular relaxation processes) were analyzed using generalized relaxation functions, to determine if the dielectric response is dominated whether by mobile or bound charge carriers, or by the conductivity contribution or molecular relaxation processes.

Introduction of synthetic polymers in recycled polyethylene terephtalate matrix does not influence the dialectical properties of that.

It was deduced that ionic and electronic charge carriers have in principle a similar frequency and temperature dependence and electrode polarization effects are expected only for materials with a high concentration of ionic charge.

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