DIELECTRIC RELAXATION SPECTROSCOPY OF POLYETHYLENE/LIGNOCELLULOSIC POLYMERS BLENDS

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Abstract: Polymer blends of recycled high density poly(ethylene) (RPE) and wood flour (WF) have been prepared by using 3 types of compatibilizing agents. Dielectric relaxation spectroscopy measurements have been carried out by performing temperature sweeps at constant frequency and frequency sweeps at constant temperature. Incorporation of natural polymers and compatibilizing agent in the polyolefin matrix leads to an increase of conductivity and consequently of the dielectric loss values when comparing with those of matrix.

I. Introduction

Natural and wood fiber reinforced composites are the fastest-growing segment in the overall composites industry. Demand for these ecology-oriented materials, which can easily be recycled, will grow to $1 billion by 2007 driven by growth in automotive applications and in furniture, design and building industries [1].

For the effective processing of these composites we need a reliable, rapid, safer and stable process control. Dielectric relaxation spectroscopy (DRS) and mechanical properties are excellent methods for such applications in polymer process analysis. The aim of the present work is to show that these both methods are outstandingly suitable for the in-line determination of the composition of natural fiber reinforced composites and nanocomposites during extrusion processes.

II. Experimental program

A. Materials

As a polymer matrix recycled polyethylene (RPE) in the shape of powder with 0.17 g/min. flow index (at the 190°C temperature and with the 2.16 kg. weights) obtained by recycling the packages for bottle drinks was used. As filling material hardwood wood flour (WF) from furniture industry waste was used.

In order to achieve a better compatibility between the matrix and the filling material the following three compatibilizing agents supplied by EXXON CHEMICAL, were used: copolymer ethylene-propylene nonmodified with 77% ethylene [PE 805 (C1)]; copolymer copolymer ethylene-propylene modified with 0.3% maleic anhydride [Exxelor VA 1820 (C2)]; ethylene-propylene modified with 0.7% maleic anhydride [Exxelor VA 1803 (C3)];

B. Method of work

Composites were obtained by mixing RPE with hardwood flour and the compatibilising agent. The method was presented before in other article [2]. The extruder has a single screw with the diameter of 19 mm and the length/diameter ratio=25 and the temperature profile were over to 130°C-145°C

Composite materials were obtained by an experimental program presented in **Table 1**.

Table 1. Experimental program

Sample Code	RPE, %	WF, %	C1, %	C2, %	C3, %
RPE	**100**	**-**	**-**	**-**	**-**
A1	**77**	**20**	**-**	**-**	**3**
A2	**72**	**25**	**-**	**-**	**3**
A3	**67**	**30**	**-**	**-**	**3**
B1	**80**	**20**	**-**	**-**	**-**
B2	**77**	**20**	**3**	**-**	**-**
B3	**77**	**20**	**-**	**3**	**-**

After the composites granules were obtained, these were rolled and heat pressed processed in small plates of 1x235x235mm (thickness x width x length) at a 150°C temperature, and a 150 bar pressure in 40 minutes. From these plates dumb bells type test samples were made with 1.35x10x90 mm active section dimensions which will be tested to a physics-mechanics trial.

C. Investigation Methods

In our study, DRS measurements of the composite materials were carried out in a Novocontrol Alpha high-resolution dielectric analyzer that covers a frequency range between 3 μHz and 10 MHz. The instrument is interfaced to a computer and equipped with a Novocontrol Novocool cryogenic system for the temperature control. The analyzer has been used to measure the complex dielectric permittivity during temperature sweeps at constant frequency of 1 kHz and frequency sweeps at constant temperarature of 25°C.The dielectric response of a material can be expressed by a complex relative dielectric permittivity:

$$\varepsilon^{*}(\omega) = \varepsilon' - i\varepsilon'' \quad (1)$$

Where ε' is the capacitive component or dielectric permittivity and ε'' is the resisitive one or dielectric loss. In the analyzed frequency range the dielectric loss presents a dipolar ε_p'' component and a conductive ε_c'' one [3, 4]. The ionic conductivity due to charge migration can be calculated from the conductive component of loss:

$$\sigma = \omega\varepsilon_0\varepsilon_c'' \quad (2)$$

The evolution of dielectric loss and conductivity with temperature at a fixed frequency and with frequency at a fixed temperature are analyzed. Mechanical characteristics of composites were determined with a testing machine TIRATEST 2200 Germany according to STAS 6642-73. Measurements were made to a 100 mm/min. pulling speed. Before analyzing the samples, these were conditioned by maintaining then into a vacuum oven for three hours to 50°C and 0.01 kgf/cm^2 pressures. For each sample a number of 5 determinations were made, and their mean was considered the final result. The impact strength has been evaluated on notched samples in IZOD mode using a testing machine Complete Izod Pendulum 540/228062 Germany according to STAS 7310-87.

III. Results and Discussions

It is well known, that the dielectric constant and conductivity depend on the temperature and frequency range of the applied electrical field.

An overview of the temperature sweeps for RPE/WF blends at a constant frequency of 1 kHz is shown in Fig. 1-6.

Due to the (electrically) inhomogeneous nature of the polymer blends and the introduction of an additional compatibilizing agent the conductivity and dielectric loss should appear very affected respect those for the matrix.

One relaxation process can be identified in the RPE matrix (the intra crystalline α process), Fig. 1a while its conductivity remains almost constant up to 40-60°C, for slowly decreasing at higher temperatures (Fig. 1b).

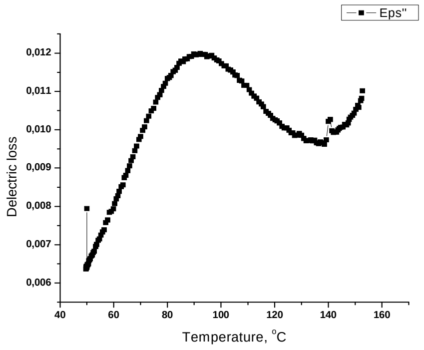

Fig.1a. Temperature dependence of the dielectric loss for RPE

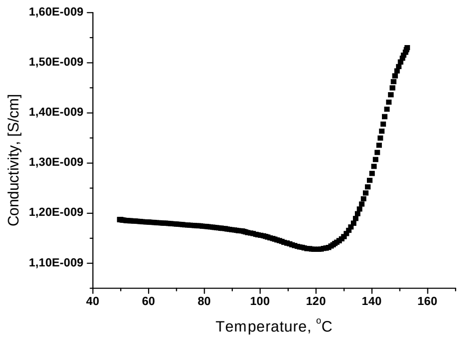

Fig.1b. Temperature dependence of the conductivity for RPE

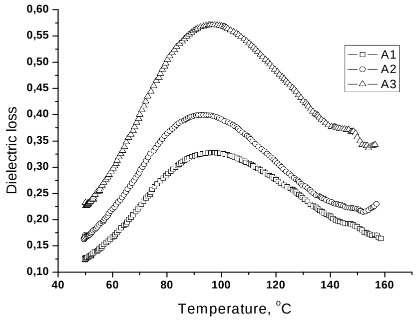

Fig.2a. Temperature dependence of the dielectric loss for blends RPE/WF with different amount of WF

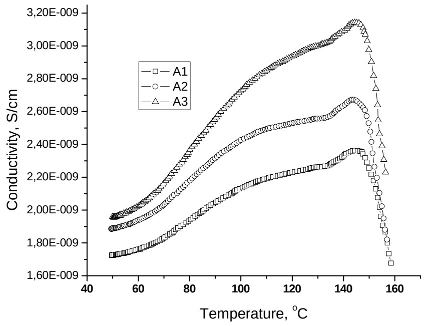

Fig.2b. Temperature dependence of the conductivity for blends RPE/WF with different amount of WF

Both cellulose dipolar structures present in wood flour and compatibilising agent actions can be the cause of the increase of the conductivity in the compound, together with the interfacial effects created between components.

The conductivity of RPE/WF blends increases proportionally with temperature and amount of wood flour (Fig. 2b). Temperature increases ionic conductivity by increasing the mobility of ions. The increase due to wood flour probably is due to its flour crystalin-amorph structure.

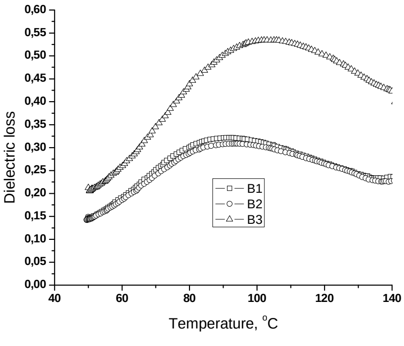

Fig.3a. Temperature dependence of the dielectric loss for blends RPE/WF with different compatibilizing agents

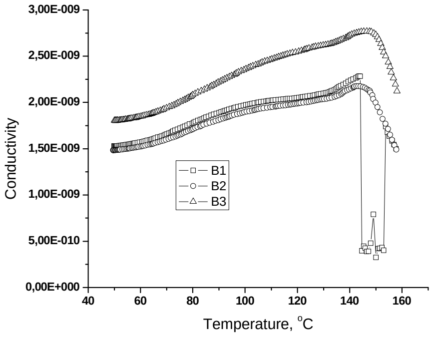

Fig.3b. Temperature dependence of the conductivity for blends RPE/WF with different compatibilizing agents

For blends with RPE, wood flour and C3 the peak in dielectric loss (the maximum of the relaxation) is centered at 95°C, similar than that for RPE, but dielectric loss values appearing much higher for the blends with natural polymers.

The presence of the maleic anhydride in C2 compatibilizing agent (sample B3) leads to a increase of the dielectric loss probably due to its structure, which allows electron migration in the amorphous zone.

Inclusion of the wood flour in polyolefinics matrix leads to modification of the dielectrical parameters in to a large domain. And for this reason evaluation of this are necesary.

Obtained experimental data are corelated and discussed in comparison with dielectrical characteristics of the recycled polyethylene matrix (RPE).

Modification of the permittivity (ε_r) and dielectric losses (tg δ) of the recycled polyethylene/wood flour/compatibilizing agent blends with different amount of the filler and different compatibilizing agents as function of the frequency of the applied electrical field are illustrated in the figures 4-5.

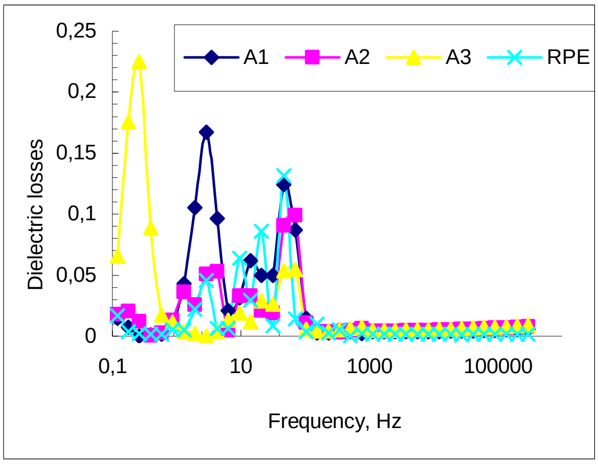

Figure 4a. Variation of the dielectric losses as function of the frequency of the applied electrical field for blends with different amount of wood

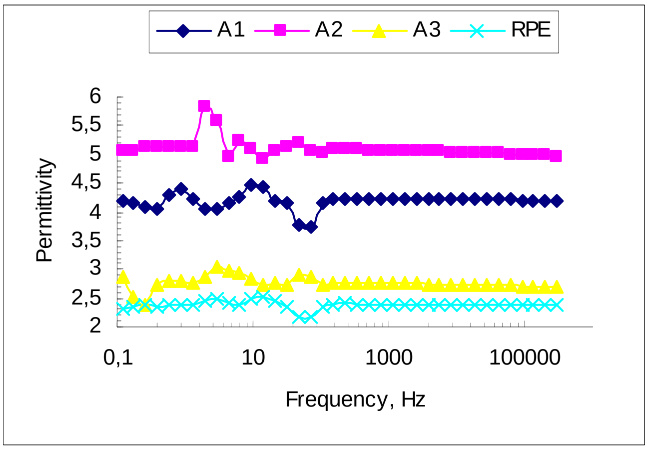

Figure 4b Variation of the permittivity as function of the frequency of the applied electrical field for blends with different amount of wood

Illustrated dielectric properties presents important modification only in 0-1200 Hz frequency range. After 100 Hz, tg δ takes very small values –electrical dipoles could not follow the rapid variation of electrical field. In this range, the addition of wood flour influences both permittivity and dielectric losses. As one can observe by the increase from 20-25 wt.% of wood flour content, permittivity increases from 4,5 to 5,8 compared with recycled polyethylene value.

This behaviour is determined by the biphasic amorphous/crystalline of the natural polymer in this range addition of wood flour influence both permittivity and dielectric losses.

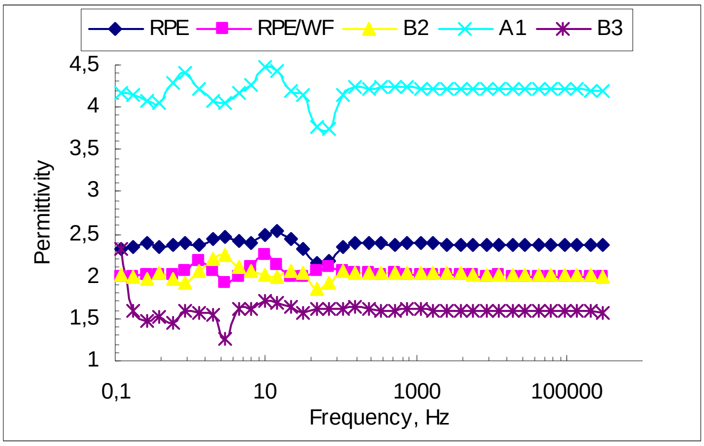

Figura 5a. Variation of the permittivity as function of the frequency of the applied electrical field for blends with different compatibilizing agents

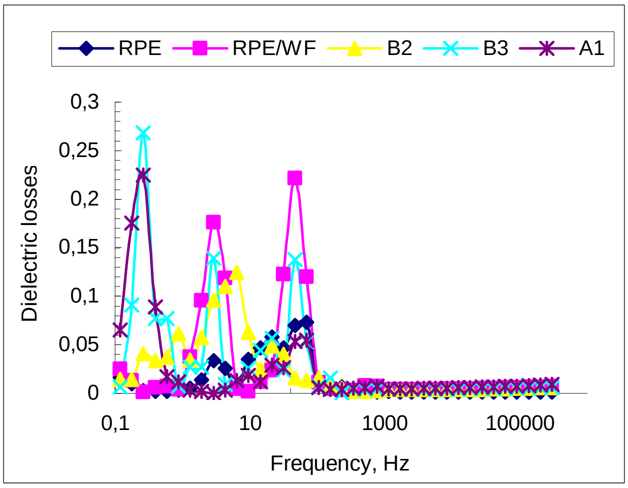

Figura 5b Variation of the dielectric losses as function of the frequency of the applied electrical field for blends with different compatibilizing agents

Permittivity of the blends with compatibilizing agents decrease exception made the compatibilizing agent C1803 with 0.7 % maleic anhydride, for that the value of permittivity is 4.2 in comparison with 2.3 for recycled polyethylene.

The mechanical properties, elastic modulus (E), breaking strength (σ), maximum breaking strength (σ_m), elongation at break (ε), maximum elongation at break (ε_m), total elongation (ε_t), impact strength (IZOD) and melt flow index (MFI) of the RPE/natural polymers reprocessed in the single screw extruder are reported in **Table 2**.

The breaking strength and elongation at break values are lower than the polymeric matrix values (RPE) but in case of the modulus of elasticity these values are much lower than that
The new created materials have a izod impact strength by 5.3-7.2 kgf.cm/cm^2 comparatively with the 9.3 kgf.cm/cm^2 RPE impact strength

These results can be due to the two different polymeric and non-polymeric phases, being known the fact that the wood flour presents strong hydrophilic properties, while the RPE polymeric matrix is hydrophobic. Another cause of having lower mechanical properties than RPE can be the lack of compatibility between the two polymer phases.

Table2. Mechanical properties of the composites obtained in experiments

Sample Code	**σ, , N/mm^2**	**σ_m, , N/mm^2**	**ε, %**	**ε_t, %**	**IZOD, kgf.cm/cm^2**	**E, N/mm^2**
RPE	168.5	186.4	17.61	10.8	9.3	3051.2
A1	146.3	147.9	10.33	9.26	5.6	1988.9
A2	133.5	138.5	7.7	7.4	5.6	1471.7
A3	143.7	151.0	4.9	4.8	5.3	2375.3
B1	104.6	105.0	8.03	7.7	6.4	1165.5
B2	144.4	149.56	11.06	9.9	7.2	1604.0
B3	145.8	146,9	7.5	7.4	6.5	1613.2

In case of elongation at break and of shock resistance the new created materials presents lower values than those determined for the recycled polyethylene, but from three compatibilizing agents the C2 offers the higher values. The 0.7 % maleic anhydride grafted ethylene-propylene copolymer C3 has a positive influence on the composite materials elasticity modulus.

IV. Conclusions

1. The addition of natural polymers in RPE matrix does not influence the mechanical properties of the material, being interesting from the point of view of several application fields like construction, car industry, family use;
2. All compatibilizing agents lead to increase of the RPE/natural polymer conductivity. The highest values were obtained for the case of RPE/wood flour blends;
3. For blends with RPE, wood flour and C3, the maximum of dielectric loss is centered at 95°C, very similar to that for neat RPE, but the dielectric loss values are much bigger for blends with WF due to the increase in conductivity;
4. Due to the (electrically) inhomogeneous nature of the polymer blends and the introduction of an additional compatibilizing agent the conductivity and dielectric loss appear like the most affected dielectrical properties;
5. RPE/natural polymers blends conductivity increases proportionally with temperature and amount of natural polymers;

V. References

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[2] Constantinescu G., Popa V.I.,. Popa N, Lazar N., „Composites from recycled wood and plastic", *Environmental, Engineering and Management J.*, 3(3), 405-414, 2004;
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