

Dielectric characteristics of various polymers (PVC, HDPE, EVA, PP, PS, PA and ABS) reinforced with end-of-life tires (GTR)

R. Mujal-Rosas^a, M. Marin-Genesca^b, X. Colom-Fajula^c, X. Salueña-Berna^d

^aDept. Ingeniería Eléctrica, ESEIAAT-UPC, Colom,1 Terrassa - 08222 Spain

^bDept. Ingeniería Mecánica, ETSEQ-URV, Avd. RV, Tarragona - 43007 Spain

^cDept. Ingeniería Química, ESEIAAT-UPC, Colom,1 Terrassa - 08222 Spain

^dDept. Ingeniería Mecánica, ESEIAAT-UPC, Colom 1, Terrassa - 08222 Spain.

Características dieléctricas de varios polímeros (PVC, HDPE, EVA, PP, PS, PA y ABS) reforzado con neumáticos fuera de uso (GTR)

Característiques dielèctrics de diversos polímers (PVC, HDPE, EVA, PP, PS, PA i ABS) reforçats amb pneumàtics fora d'ús (GTR)

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ABSTRACT

The massive storage of reused tires constitutes a serious environmental problem. This article focuses on finding a new application for these reused tires (GTR), and for this, the dust from the reused tires has been mixed with different thermoplastic polymers such as Polyvinyl Chloride (PVC), High Density Polyethylene (HDPE), Ethylene Vinyl Acetate (EVA), Polypropylene (PP), Acrylonitrile Butadiene Styrene (ABS), Polystyrene (PS) and Polyamide (PA), checking until the concentration values in GTR allow these new compounds maintaining its dielectric properties within acceptable values, and therefore, its possible industrial applications in the manufacture of insulators for electrical cables. Specifically, the dust from reused tires and with a particle size less than 200 μm , has been mixed with the polymers with four concentrations 5%, 10%, 20% and 50% in GTR, analyzing conductivity, permittivity, dielectric loss factor, dielectric relaxations, etc. in a temperature range of 30°C to 120°C, and with frequencies of 1·10⁻² Hz, up to 3·10⁶Hz. Finally, the fracture surfaces of the samples have been evaluated by scanning electron microscopy (SEM).

Keywords: thermoplastic polymers (PVC; HDPE, EVA, PP, ABS; PS; PA), polymer+GTR composites, dielectric properties; industrial applications.

RESUMEN

El masivo almacenamiento de los neumáticos reutilizados constituye un grave problema medioambiental. Este artículo se centra en buscar una nueva aplicación para estos neumáticos reutilizados (GTR), y para ello, se ha mezclado el polvo de los neumáticos reutilizados con diferentes polímeros termoplásticos como son el Policloruro de Vinilo (PVC), el Polietileno de Alta Densidad (HDPE), el Etileno Acetato de Vinilo (EVA), el Polipropileno (PP), el Acrilonitrilo Butadieno Estireno (ABS), el Poliestireno (PS) y la Poliamida (PA), comprobando hasta que valores de concentración en GTR admiten estos nuevos compuestos manteniendo dentro de unos valores aceptables sus propiedades dieléctricas, y por tanto, sus posibles aplicaciones industriales en la fabricación de aislantes para cables eléctricos. Concretamente, el polvo de los neumáticos reutilizados y con un tamaño de partícula inferior a 200 μm , ha sido mezclado con los polímeros con cuatro concentraciones 5%, 10%, 20% y 50% en GTR, analizándose la conductividad, la permitividad, el factor de pérdidas dieléctricas, las relajaciones dieléctricas, etc. en un rango de temperaturas de 30°C hasta 120°C, y con unas frecuencias de 1·10⁻² Hz, hasta 3·10⁶Hz. Finalmente, las superficies de fractura de las muestras han sido evaluadas por microscopía electrónica de barrido (SEM).

Palabra clave: polímeros termoplásticos (PVC; HDPE, EVA, PP, ABS; PS; PA), compuestos polímero+GTR, propiedades dieléctricas; aplicaciones industriales.



*Corresponding author: ramon.mujal@upc.edu

RESUM

El massiu emmagatzematge dels pneumàtics reutilitzats constitueix un greu problema mediambiental. Aquest article se centra a buscar una nova aplicació per a aquests pneumàtics reutilitzats (GTR), i per això s'ha barrejat la pols dels pneumàtics reutilitzats amb diferents polímers termoplàstics com són el Policlorur de Vinil (PVC), el Polietilè d'Alta Densitat (HDPE), l'Etilè Acetat de Vinil (EVA), el polipropilè (PP), l'Acrilonitril Butadiè Estirè (ABS), el Poliestirè (PS) i la Poliamida (PA), comprovant fins a quins valors de concentració en GTR admeten aquests nous compostos, mantenint dins d'uns valors acceptables les seues propietats dielèctriques, i per tant, les seves possibles aplicacions industrials en la fabricació d'aïllants per a cables elèctrics. Concretament, la pols dels pneumàtics reutilitzats i amb una mida de partícula inferior a 200 µm, ha estat barrejada amb els polímers amb quatre concentracions 5%, 10%, 20% i 50% en GTR analitzant la conductivitat, la permitivitat, el factor de pèrdues dielèctrics, les relaxacions dielèctriques, etc. en un rang de temperatures de 30°C fins a 120°C, i amb unes freqüències de 1·10⁻² Hz, fins a 3·10⁶Hz. Finalment, les superfícies de fractura de les mostres han estat avaluades per microscòpia electrònica d'escombrada (SEM).

Paraules clau: polímers termoplàstics (PVC; HDPE, EVA, PP, ABS; PS; PA), compostos polímer+GTR, propietats dielèctriques; aplicacions industrials.

1. INTRODUCTION

The important problem of the accumulation of used tires¹⁻³ has driven efforts to find solutions for their recovery and reuse. Many plastic materials include elastomers to improve their toughness. In general, a thermoplastic polymer acts as a matrix and the elastomer as a dispersed phase⁴⁻⁸. In the case of recycled elastomers, when mixed with thermoplastic polymers the expected compatibility is low, and this compatibility can be increased by reducing the degree of cross-linking of the GTR through devulcanization⁹⁻¹². Another way to increase interfacial bonding is through pretreatment with acids¹³⁻¹⁶, although this is not very effective. More significant changes are observed in the properties of the compounds if we vary the size of the reinforcement particles, this being the alternative applied in this publication^{17,18}, in which seven polymers are mixed: PVC, HDPE, EVA, PP, ABS, PS, and PA with GTR with a single particle size less than 200µm, and four concentrations (5%, 10%, 20% and 50%), analyzing up to which concentration it is possible to load the polymers without affecting their dielectric and thermal properties initial microstructure¹⁹⁻²².

2. METHODOLOGY

2.1 Materials

The thermoplastic polymers used are: polyvinyl chloride (PVC); high-density polyethylene (HDPE) recycled

from water bottles; the EVA copolymer (Ethylene Vinyl Acetate), indicated for the production of films and coatings by extrusion (18% vinyl acetate and 82% ethylene); polypropylene (PP); acrylonitrile butadiene-styrene (ABS), composed of 30% acrylonitrile, 20% butadiene and 50% styrene, an amorphous thermoplastic material, very resistant to impact; polyamide 6 (PA 6), known as nylon 6, a semi-crystalline material, transparent solid, hard, brittle and impact resistant; and polystyrene (PS), an amorphous, hard and brittle material, very resistant to impact. Table 1, shows a summary of relevant properties of these seven polymers.

Table 1. Commercial name, fluidity index, density four each material.

Polymer Type	Commercial Name	Fluidity Index or Melt Flow Index (g/min)	Density (kg m ⁻³)
PVC	Etinox	1.35	1.225
EVA	Alcudia PA 539 type	0.20	937
HDPE	Alcudia 4810-B	1.35	960
PA 6	Ultramid B3S	1.55	1130
ABS	Terluran® HH-106	1.45	1050
PP	Isplen® 099 K2M type	0.55	902
PS	Polystyrol 486 M	1.45	1050

Finally, the out-of-use tire (GTR), with a size smaller than 700µm supplied by Alfredo Mesalles (Spain), was verified through analysis with the TGA that its carbon black content is 35%. The original GTR was separated by sieving to a size less than 200 µm.

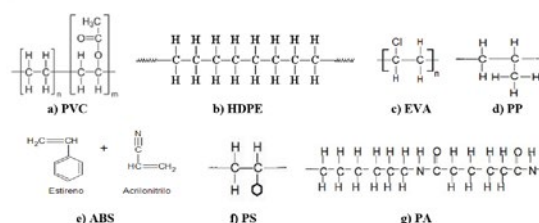


Figure 1. Chemical structures of the polymers used.

2.2 Compound Preparation

The dust from the reused tires was dried in an oven at 100°C for 24h. For the particle size $p < 200\mu\text{m}$, six samples of the compounds were prepared varying their composition from 5%, 10%, 20% and 50% in GTR. The mixing process was carried out with a Brabender machine, type EHT PL, at different temperatures and with limited mixing times: 195°C and 5min for PVC; 153°C and 4min for HDPE; 105°C and 4min for EVA; 165°C and 4min for PP; 180°C and 4min for ABS; 185°C and 4min for PS; and 200°C 8min for PA, to avoid degradation of the polymers. The Polymer/GTR laminates (170 x 170 x 2mm³) were obtained using a Collin Mod. P 200E hot plate press, at 100kN, for about 10 min. at temperatures of 210°C (PVC), 170°C (HDPE), 120°C (EVA), 180°C (PP), 200°C (ABS), 195°C (PS) and 210°C (PA). The cooling stage was carried out with a closed circuit of running water, which was carried out in the same press and at the same pressure for 5 min. The samples for testing were properly configured in accordance with the specifications of ASTM-D-412-98.

Table 2. Glass transition temperature, melting temperature, and % Crystallinity, for each material.

% de GTR	Tg1 (°C)	Tg2 (°C)	Tf °C	crystallinity γ (%)	% de GTR	Tg1 (°C)	Tg2 (°C)	Tf °C	crystallinity γ (%)
EVA + 0 %			90.0	29.2	PA + 0 %	31		227	38.1
EVA + 5 %			88.0	29.0	PA + 5 %	33		227	39.6
EVA + 10 %			87.8	29.2	PA + 10 %	35		227	36.7
EVA + 20 %			88.8	28.5	PA + 20 %	36		226	36.6
EVA + 50 %			87.1	29.0	PA + 50 %	38		224	33.8
HDPE + 0 %			137.0	70.3	PVC + 0 %	83.0			
HDPE + 5 %			135.0	68.1	PVC + 5 %	82.5			
HDPE + 10 %			135.2	69.7	PVC + 10 %	82.0			
HDPE + 20 %			135.0	69.1	PVC + 20 %	82.2			
HDPE + 50 %			132.0	78.0	PVC + 50 %	80.2			
PP + 0 %			171.2	42.1	ABS + 0 %	106.2	125.5		
PP + 5 %			171	41.7	ABS + 5 %	106.7	124.6		
PP + 10 %			171	41.6	ABS + 10 %	106.2	123.4		
PP + 20 %			170.8	40.2	ABS + 20 %	106.4	124.4		
PP + 50 %			168.5	42.0	ABS + 50 %	105.9	123.6		

2.3 Scanning Electron Microscopy (SEM)

The SEM was used to analyze the fracture surface of the broken samples in the Strain-Tensile tests. By observing the environment of the reinforcing particles, it is possible to analyze the effects of this filler material on the matrix. Some images of the samples have been analyzed depending on the compound and the concentration in GTR. The microscope used was a JEOL 5610, and the samples were coated with a thin layer of gold to increase their conductivity.

2.4 Electrical Dynamic Analysis (DEA)

The dielectric analysis was also carried out with particles smaller than 200 μm , as these offer the best results in all previous tests. The dielectric magnitudes were measured using a Dynamic Electrical Analysis (DEA) with the BDS40 equipment, which incorporates a Novotherm temperature sensor from Novocontrol, using a 2cm diameter compression mold. The measurements were taken in a frequency range between $1 \cdot 10^{-2}$ Hz and $3 \cdot 10^6$ Hz, with a temperature variation between 30°C and 120°C, and at a speed of 3°C/min, using parallel plate sensors.

3. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy

Some SEM microphotographs of the fracture surface from the Strain-Tensile Test^{23,24} of the polymer/

GTR specimens, with a particle size $p < 200 \mu\text{m}$, and a concentration of 10% in GTR, are shown in Figure 2. The particles of GTR do not reach their degradation temperature when mixing, clearly observing these particles dispersed in the homogeneous medium of the polymer matrix, which does reach the melting temperature. The result is a microgranulated mass with a degree of dispersion that depends on the mixing time and temperature, which does not facilitate cohesion between phases.

In general, for low concentrations¹⁷⁻¹⁸, the reinforcing particles are integrated and covered by the matrix. The topology in the amorphous region of the matrices, including the interconnection between crystalline sheets, shows good interfacial adhesion. Small, cleanly cut areas are seen, which indicates that the particles have broken before being released in the tensile test. Likewise, the formation of superstructures with homogeneous morphologies is observed.

3.4 Electrical Properties

The comparative dielectric analysis has been carried out at different frequencies and temperatures for all the compounds, with the GTR particles of sizes less than 200 μm . With the dielectric spectroscopy technique used, the samples are subjected to an alternating voltage of variable frequency and from the impedance measurement the dielectric magnitudes of the material are obtained. In the alternating current regime, the relative permittivity is a complex number whose real

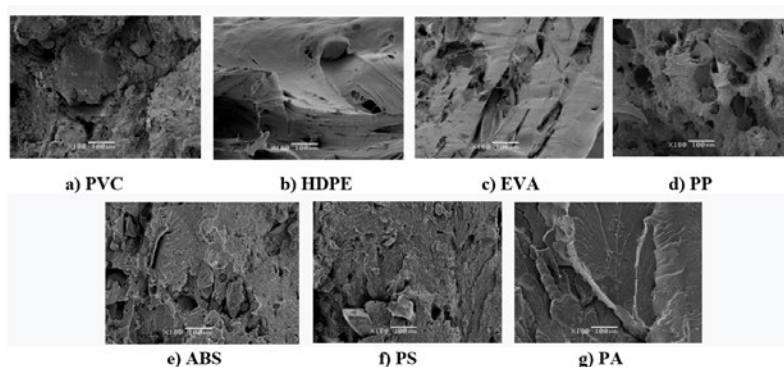


Figure 2. SEM micrographs of the Polymers/GTR, for a concentration of 10% of Polymer/GTR and particle size $< 200 \mu\text{m}$. a) PVC/GTR; b) HDPE/GTR; c) EVA/GTR; d) PP/GTR; e) ABS/GTR; f) PS/GTR; g) PA/GTR

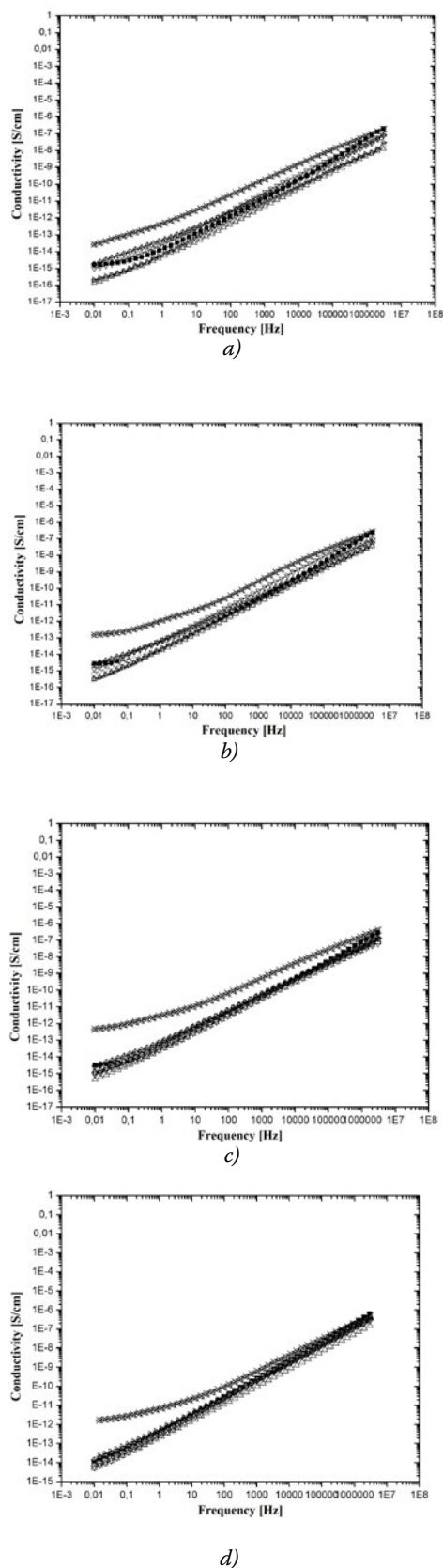


Figure 3. Conductivity (σ) at 30°C, as a function of frequency: a) compound+5% GTR. b) compound+10% GTR, c) compound+20% GTR, d) compound+50% GTR: • EVA; ◻ HDPE; ◻ PP; ▽ PVC; ◊ ABS; ✕ PA; ◻ PS.

part, ϵ' , is proportional to the energy stored in each cycle, while the imaginary part, ϵ'' , is proportional to the energy lost and is known as loss factor. Through the analysis of the real permittivity and the loss factor with frequency and temperature, relaxations of the material can be determined and, therefore, information about the structure, transitions with temperature, the effect of the addition of particles reinforcement, etc., of the sample studied. For the same material, the relaxations observed are called, α , β , γ and ρ , according to the order in which they appear when going from low to high temperatures. In the frequency and temperature regime studied, it is the case that only relaxations α and β appear. However, this label refers only to the order in which they appear for a given material; The origin and properties of each α , and β relaxation depend on the polymer in question.

3.4.1 Conductivity (σ)

Figures 3.a, 3.b, 3.c and 3.d show the results of the conductivity (σ), as a function of frequency, for four concentrations in GTR (5%, 10%; 20%, 50%), and a 30°C temperature.

It is observed that for low frequencies (0.01Hz) and concentrations of 5% of GTR, the four most amorphous compounds PVC, PS, ABS²⁵⁻²⁸ and EVA^{29,30,31}, show conductivities of around $1 \cdot 10^{-15}$ S/cm, while HDPE (semi-crystalline)^{18,32}, and PP (more crystalline)³¹, have conductivity values of $1 \cdot 10^{-16}$ S/cm, finally PA is the most conductive with values of $1 \cdot 10^{-14}$ S/cm.

With the increase of GTR (at 30°C), the conductive behavior of the samples, in most of the cases analyzed, increases. With 10% in GTR, the conductive behavior is more heterogeneous, with PS and PP being the least conductive. For PS and PP with 5% GTR, at 50Hz there are some conductivities of 10^{-13} and 10^{-11} S/cm. For 40% GTR, PS is revealed as the most insulating material (10^{-14} S/cm) followed by ABS, for which, at industrial frequency (50 Hz), a conductivity of 10^{-10} S/cm is observed.

The most resistive without GTR are HDPE, PS and PP, followed by EVA, PVC and ABS. Thus, it is observed that with the addition of GTR, the conductive behavior of almost all polymers tends to converge, except in the case of PA, which remains two orders of magnitude above the rest of the polymers analyzed, that is, for 40-50%, PA: $4.95 \cdot 10^{-13}$ and $1.73 \cdot 10^{-12}$ S/cm, and for the rest of the polymers, 10^{-15} S/cm, and in the case of ABS and PS, for 40% of GTR, reach conductivities of $1.05 \cdot 10^{-14}$ and $1.32 \cdot 10^{-14}$ S/cm, respectively. These results can be interpreted as compounds with worse electrical behavior with carbon black (CB)^{28,29}.

If the temperature is increased to 120°C (figures 4.a, 4.b, 4.c and 4.d) the behavior of the compounds differs depending on their degree of crystallinity. Thus, for the most amorphous materials (PVC/PS/ABS/EVA + GTR), two clearly differentiated zones appear in this frequency range: one at low frequencies, up to about 100Hz, and another at frequencies above 100Hz. In the low frequency zone, the conductivity remains constant and increases with the GTR content (at 0.01 Hz), on the contrary, from 100Hz the dependence is linear on

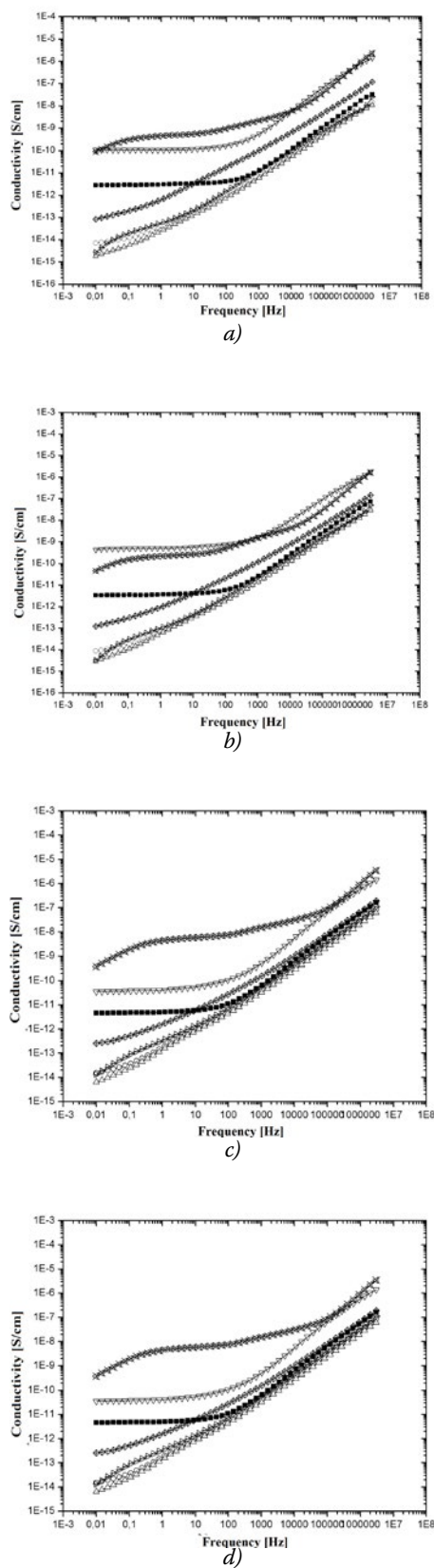


Figure 4. Conductivity (σ) at 120°C, as a function of frequency: a) compound+5% GTR. b) compound+10% GTR, c) compound+20% GTR, d) compound+50% GTR: • EVA; ◦ HDPE; Δ PP; ▽ PVC; ◊ ABS; ⋈ PA; ▴ PS.

a logarithmic scale, becoming practically independent for PVC/GTR.

For the most crystalline materials (HDPE, PA and PP), and in this frequency range, the zone in which the conductivity is independent of the frequency does not appear, although a slight change in behavior can be sensed at frequencies of the order of 0.01Hz, this change being more significant for HDPE/GTR than for PP/GTR, as the latter is more crystalline. As León²⁷ describes, this behavior is consistent with a sublinear dispersive conductivity of the type:

$$\sigma = \sigma_0 + A\omega^n \quad (1)$$

where σ_0 , is the conductivity in direct current (DC), is the pulsation, f is the frequency, and A and n are factors that take values between 0 and 1, and that depend on the temperature, the material and the GTR content. This relationship is known as universal dynamic response and is typical of materials with a high degree of disorder, such as PVC, PS, ABS and EVA, and to a lesser extent, HDPE, PA and PP. The frequency ranges that separates both zones moves towards higher values with temperature, this transition not being observed in Figure 3, since the area that corresponds to the DC regime is not shown for the frequency range studied. At 120°C, the conductivity at low frequencies has increased for PVC/PS/ABS/EVA + GTR and all concentrations in GTR, between three and four orders of magnitude on average (from $1 \cdot 10^{-15}$ S/cm to $1 \cdot 10^{-10}$ S/cm for PVC/GTR and from $1 \cdot 10^{-14}$ S/cm to $1 \cdot 10^{-11}$ S/cm for EVA/GTR), basically due to the increase in continuous conductivity (DC). While this increase is one or two orders of magnitude on average (from $1 \cdot 10^{-13}$ S/cm to $1 \cdot 10^{-10}$ S/cm for HDPE+GTR or PA+GTR and from $1 \cdot 10^{-14}$ S/cm to $1 \cdot 10^{-13}$ S/cm for PP/GTR) for more crystalline materials such as HDPE, PA and PP. For high frequencies the increase in conductivity with temperature is much smaller, being less than an order of magnitude in all cases (from $1 \cdot 10^{-7}$ S/cm to $1 \cdot 10^{-6}$ S/cm). In the case of PVC/GTR, the conductivity increases significantly with carbon black to inflect at a point at which it tends asymptotically to the limit conductivity that varies depending on the case.

3.4.2. Permittivity and Loss Factor

Figures 5.a, 5.b, 5.c, and 5.d show the values of the real permittivity (ϵ') as a function of frequency for each polymer and the three concentrations in GTR (10%; 20%, 50%), and at a temperature of 30°C.

The material with the highest real permittivity is polyamide, which without GTR additives and up to 10% GTR presents values of 10 for low frequencies, and it can be deduced that the addition of GTR affects the real permittivity, since it increases up to 3 orders of magnitude. For polar materials (PVC, ABS, PS and EVA), the permittivity is influenced by the GTR content, increasing with concentration and this increase being more noticeable at low frequencies and concentrations higher than 20% in GTR (at 0.01 Hz and 5% in GTR, the permittivity is 3.5 for both PVC/GTR^{33,34,35} and EVA/

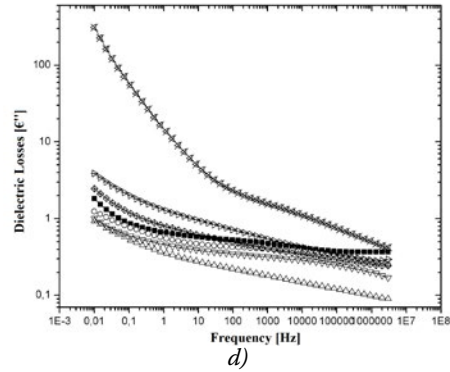
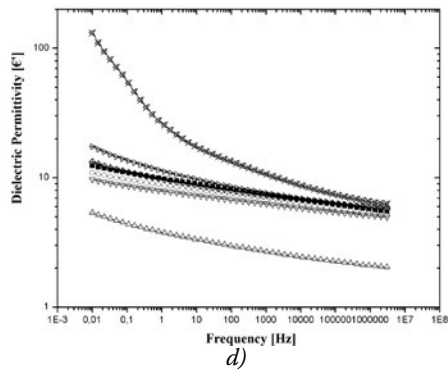
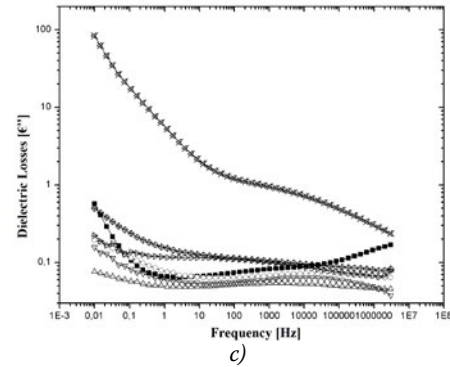
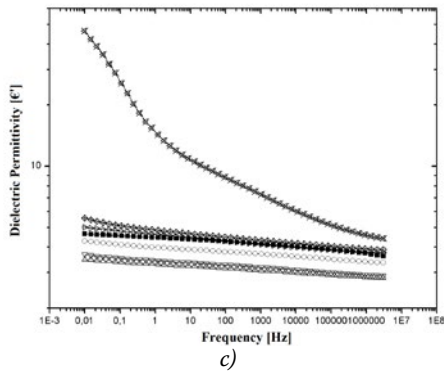
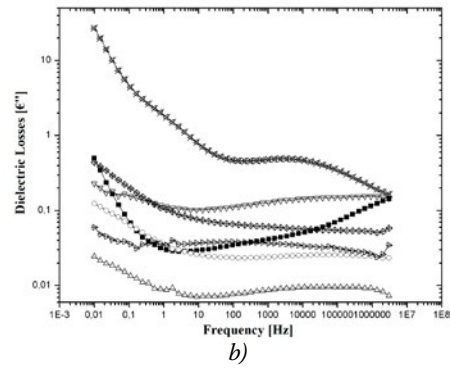
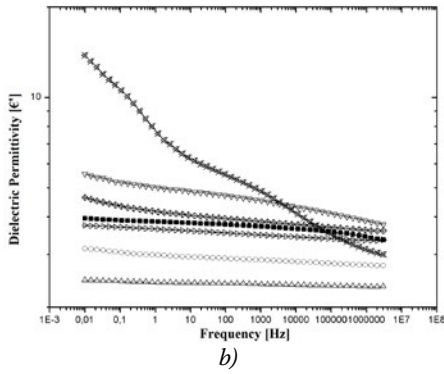
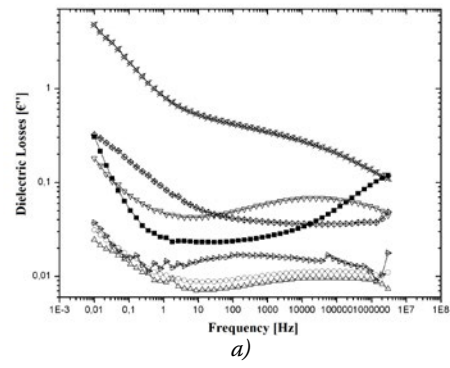
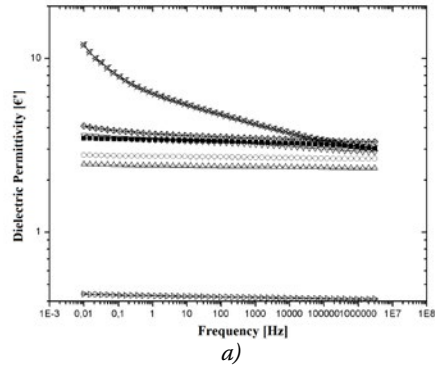


Figure 5. Dielectric permittivity (ϵ') at 30°C, as a function of frequency: a) compound+5% GTR. b) compound+10% GTR, c) compound+20% GTR, d) compound+50% GTR: • EVA; ◦ HDPE; Δ PP; ▽ PVC; ◇ ABS; ⋈ PA; ▷ PS.

Figure 6. Dielectric losses (ϵ'') at 30°C, depending on frequency: a) compound+5% GTR. b) compound+10% GTR, c) compound+20% GTR, d) compound+50% GTR: • EVA; ◦ HDPE; Δ PP; ▽ PVC; ◇ ABS; ⋈ PA; ▷ PS.

GTR³⁶. For concentrations of 40% in GTR and the same frequency, the permittivity values are 10, and 13 for PS/GTR and ABS/GTR respectively. On the other hand, the frequency negatively influences the permittivity, decreasing its value due to dielectric dispersion and decreasing the differences between the compounds (at a frequency of $1 \cdot 10^7$ Hz, and concentrations of 10% and 40% in GTR, the permittivity values are 2.8 and 4.8 for PVC/GTR, and 3 and 5.5 for ABS/GTR)³⁶.

For non-polar materials (HDPE and PP), the real permittivity increases as the GTR content increases, this increase being more significant at low frequencies. Thus for 0.01Hz and 5% in GTR, the permittivity is 2.8 and 2.4 for HDPE/GTR^{37,38,39} and PP/GTR⁴ respectively, while for concentrations of 40% in GTR and the same frequency, the values of permittivity are 11 and 6 for HDPE/GTR and PP/GTR respectively. Regarding the influence of frequency, permittivity decreases with increases in frequency, mainly due to dielectric dispersion. As HDPE, PA and PP are not polar materials, only GTR contributes to this phenomenon, this trend being less significant with low concentrations of GTR, and becoming null in the case of pure materials. For a frequency of $1 \cdot 10^7$ Hz, and concentration of 5%, the permittivity value is 2.1 for both HDPE/GTR; PA/GTR as for PP/GTR, while for 40% in GTR the values are 5 and 3 for the same compounds.

Figures 6.a, 6.b, 6.c, and 6.d show the values of the imaginary permittivity (ϵ'') as a function of frequency for the various compounds with four concentrations in GTR (5%, 10%; 20%, 40%), and at 30°C temperature.

For polar materials (PVC, PS, ABS and EVA), the loss factor is influenced by the GTR content, increasing its value when the concentration increases (at 0.01Hz and 5% in GTR, the values of the losses are 0.15 and 0.3 for PVC/GTR and EVA/GTR respectively, while, for the same frequency, but with 50% in GTR, the values for PVC/GTR and EVA/GTR are respectively 1 and 2). In all samples for the PVC/GTR composite, the losses decrease rapidly in the low frequency region up to about 10Hz, and then increase and pass through a maximum located between $1 \cdot 10^4$ Hz and $1 \cdot 10^5$ Hz. This change in slope that is observed at this frequency and temperature for the loss factor is known as α relaxation and is linked to the local movements of the main chain. α relaxation in PVC has been studied by Ishida et al.³⁴. For non-polar materials (HDPE, PA and PP), the loss factor increases with increases in GTR concentration, these increases being more noticeable at low frequencies. Thus at 0.01Hz and 5% in GTR, the dielectric losses (ϵ'') are 0.035 and 0.028 for HDPE/GTR and PP/GTR respectively.

The influence of frequency is due to the contribution of conductance, as dielectric losses depend on conductivity (σ and initial conductivity σ_0) divided by frequency ($w=2 \cdot \pi \cdot f$), as well as interfacial phenomena that increase the loss factor at low frequencies.

$$\epsilon'' \propto \frac{\sigma}{\epsilon_0 \omega} \quad (2)$$

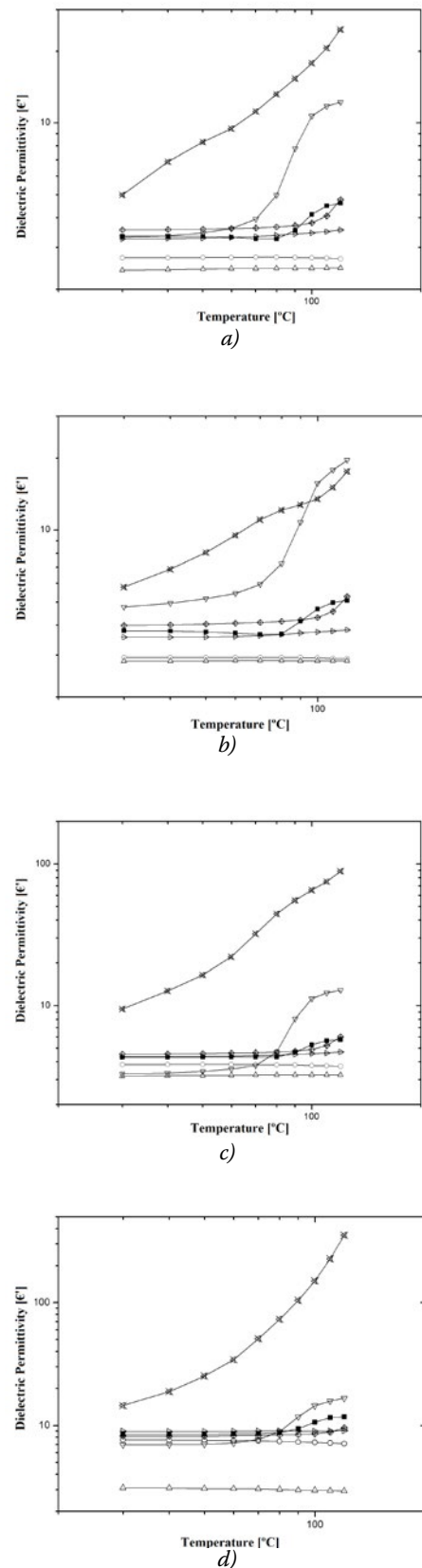


Figure 7. Dielectric permittivity (ϵ') at 50Hz, as a function of temperature: a) compound+5% GTR. b) compound+10% GTR, c) compound+20% GTR, d) compound+50% GTR: • EVA; ° HDPE; Δ PP; ▽ PVC; ◇ ABS; ⊠ PA; ◀ PS.

On the other hand, for high frequencies the HDPE/GTR has a relaxation in the imaginary permittivity ϵ'' that shows a maximum between $1 \cdot 10^3$ Hz and $1 \cdot 10^5$ Hz. This maximum can be identified with the α relaxation of the HDPE, which is related to the lateral branches in polyethylene³². As high-density polyethylene does not have many secondary branches, this relaxation is barely perceived. Also, for high frequencies and low concentrations in GTR, it is possible to observe for PP/GTR, although weakly, β relaxation peak at the imaginary permittivity ϵ'' . This peak can be identified with the α relaxation of PP, which has its origin in the amorphous regions⁴⁰.

Figures 7.a, 7.b, 7.c, and 7.d show the values of the dielectric permittivity (ϵ') at 50Hz, as a function of temperature, for the various compounds with GTR concentrations of 5%, 10%, 20%, and 50%.

In general, the increase in permittivity with temperature is due to the contribution of two mechanisms: the first, an increase in the mobility of the macromolecules, with a decrease in density that increases the permittivity, and the second, a difference of thermal expansion between the different areas of the polymer itself that reduces it^{36,40,41}. However, above the glass transition temperature T_g , the first contribution is much higher than the second, so the global permittivity increases. The presence of GTR particles accentuates both mechanisms, the result of both contributions being a significant increase in permittivity.

Analyzing first the polar materials (PVC, ABS, PS and EVA), it is observed that for the PVC/GTR and PS/GTR compounds there is a very gentle increase in permittivity up to 70°C depending on the GTR content (for 30°C the Permittivity values are 3.2 for 5% in GTR and 7 for 50% in GTR, these values are rising to 3.4 and 7.2, at 70°C and the same conditions). From this point on, there is an abrupt change in the slope that increases considerably between 80°C and 110°C (the values at 110°C and concentrations of 5% and 50% in GTR are 10.2 and 10.4 respectively), to return, from this temperature, to the initial trend, these changes are more significant for the PS. The EVA/GTR and ABS/GTR compounds behave differently, since their permittivity practically does not vary with temperature (in less than one unit in all cases), although it does vary with the concentration in GTR (from 3.5 to 8.5 for 30°C and GTR concentrations of 5% and 50% respectively), to subsequently experience a transition between two stable regimes. This transition begins at 80°C, its inflection point is between 90°C and 100°C and ends at 110°C.

For non-polar materials (HDPE, PA and PP), a moderate increase in dielectric permittivity as a function of GTR concentration is observed overall. Thus, for the extreme concentrations of 5% and 50% in GTR, the permittivity values are for HDPE/GTR from 2.5 to 7.8, and for PP/GTR from 2.25 to 5.5 respectively. In general, the permittivity decreases slightly with increases in temperature, showing a weak dependence between the two.

Figures 8.a, 8.b, 8.c, and 8.d show the values of the imaginary permittivity (ϵ'') at 50Hz, as a function of

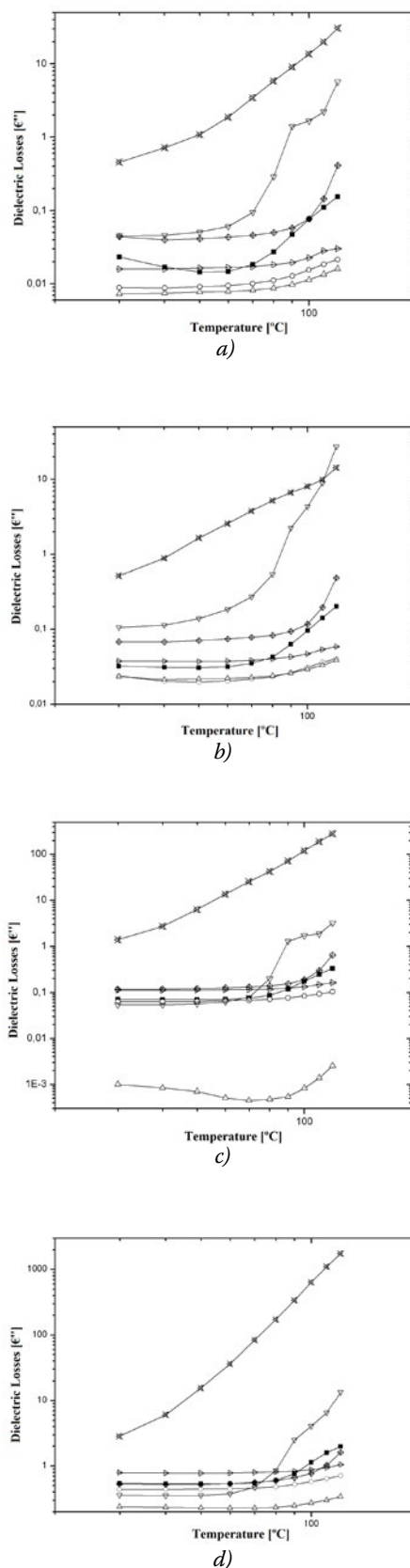


Figure 8. Dielectric losses (ϵ'') at 50Hz, as a function of temperature: a) compound+5% GTR. b) compound+10% GTR, c) compound+20% GTR, d) compound+50% GTR: • EVA; ○ HDPE; △ PP; ▽ PVC; ◇ ABS; ✕ PA; ▴ PS.

temperature, for the various compounds with four concentrations in GTR (5%, 10%, 20%, 50%).

In all materials, an increase in dielectric losses with temperature and concentration is observed. With reference to polar materials, we see that for PVC/GTR the loss factor increases from 70°C (0.045 for 5% in GTR and 0.35 for 50% in GTR) and presents a relaxation around 90°C with values for the loss factor of 1.5 for 5% in GTR and 2 for 50% in GTR, coinciding with the inflection point of the real component. This phenomenon is more noticeable with low concentrations of GTR, as also occurs in the case of α relaxation of PVC. On the other hand, near the conformation glass transition zone, the reorganization of the main chains will take place on a large scale, giving rise to α relaxation, observable at different temperatures depending on the frequency with which we work. Calorimetric measurements indicate that the glass transition temperature (T_g) is around 80°C⁴¹⁻⁴³.

With respect to the EVA/GTR, ABS/GTR and PS/GTR compounds, the behavior is similar, reducing the loss factor to a minimum at 60°C (0.02 for 5% in GTR and 0.3 for 50% in GTR), to subsequently begin to increase with temperature up to values of 0.1 and 0.7, at 120°C and concentrations of 5% and 50% in GTR, respectively. As the EVA/GTR²⁹⁻³¹ relaxation map shows, the end of β relaxation is obtained at low temperatures, while the effect of conductive processes on the loss factor ϵ'' , is observed at higher temperatures.

For non-polar materials (HDPE and PP), overall there is a slight increase in the loss factor as a function of the GTR concentration. Thus, for HDPE/GTR compounds, the loss factor ϵ'' shows an almost negligible increase as the temperature increases, its value being practically constant. As GTR is more polar and conductive than HDPE, the dielectric relaxation of the polymer matrix is masked by the properties of the filler.

With reference to PP/GTR, the behavior shows a slight initial drop in the loss factor ϵ'' up to a temperature of 70 °C, to rise from this temperature, remaining practically constant and with a value of 0.01 for 5% in GTR and 0.2 for 50% in GTR, during the rest of the analyzed spectrum. According to the relaxation map of pure PP, the low temperature region shows the end of the α relaxation, however, the α relaxation, which is related to the crystalline zone, not visible.

4. CONCLUSIONS

Regarding the microstructure, and with a single GTR particle size less than 200 μ m, it has been proven that the filler influences the microstructure of the composite causing an increase in failures in the matrix, which worsens interfacial adhesion and leads to the formation of agglomerates that cause cracks and pores of considerable size on their surface.

Regarding dielectric tests, the incorporation of GTR produces an increase in conductivity, permittivity and dielectric loss factor in all compounds. As with other similar materials, the conductivity shows a dispersive sublinear behavior in all compounds. Likewise, the

increase in conductivity is greater for low frequencies and high temperatures, regardless of the GTR content, while, for high frequencies, neither the type of material, nor the filling percentage, nor the increase in temperature, hardly they take effect.

For the PVC/GTR compound, with temperature values higher than the glass transition T_g (80°C at 50 Hz) there is a significant increase, not only in the permittivity, but also in the dielectric loss factor. These losses are considered as the combination of losses due to Maxwell-Wagner-Sillars type relaxation processes, as well as the increase in the conductivity of the compounds. At high frequencies, losses due to interfacial polarization are negligible and the dielectric behavior of the composites is governed by the losses of the polymer matrix.

The presence of a α relaxation at low temperatures and high frequencies has been detected, as well as an β relaxation with temperatures higher than T_g . The analysis of the behavior of α relaxation with temperature could indicate that the incorporation of GTR in PVC, ABS and PS significantly reduces the cooperativity of the main chains below 100°C. Both parameters are significantly influenced by the GTR content, especially above 20%.

On the other hand, for the EVA/GTR composite, the different behavior exhibited by the α relaxation peak depending on whether the temperature is lower or higher than 100°C, has given rise to a separate analysis, whose behavior is explained by the fusion of its crystalline phase.

For non-polar compounds such as HDPE/GTR and PP/GTR, permittivity tends to decrease with frequency, this decrease being more pronounced with high concentrations of GTR, and practically negligible at low concentrations. PA+GTR is the compound that has the highest values in all dielectric magnitudes, although for very high frequencies (above 100 kHz) it tends to converge with the rest of the materials, making it not suitable as a dielectric.

From the results achieved through the analysis of these compounds, only EVA+10%GTR with particle size $p < 200\mu$ m would fall within the permitted limits for insulating electrical cable covers and special motor insulation⁴⁴⁻⁴⁷.

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