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**THE INFLUENCE OF RECIPE FORMULATION AND ELECTRIC
FIELD FREQUENCY UPON DIELECTRIC LOSS IN PLASTIFIED
PVC FILMS**

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Abstract: *Plastified polyvinyl chloride (PVC) films are largely used in the clothing and footwear industries. The composition of the PVC-based blend and the curing stage determine the main characteristics of the final films. Lately, radio frequency fields (RF fields) have gained popularity as heat generators in different processing stages of polymer films, like the PVC ones. The dielectric behaviour of PVC films can be controlled by the recipe formulation of plastisol blends. This paper presents the influence of the chemical nature and concentration of some auxiliaries, added in the plastisol blend, upon dielectric loss, $\tan \delta$ in plastified PVC films obtained in high frequency electric field. The chemicals used as additives in the recipe formulation were: polydimethylsiloxane (PDMS) polymethylhydrosiloxane (PHDMS), nonylphenol ethoxylate emulsifier NF10 (NE) and collagen hydrolizate (CH). Additives concentration was in the range 4-6 parts. The RF field was provided by a high capacitive generator with 380 V supply voltage, and 13.56 MHz working frequency. Increased concentration of auxiliaries determined the increase of $\tan \delta$ irrespective the nature of the chemical auxiliary. The dielectric loss of PVC films, due to the presence of chemical additives, increased in the following order: PDMS < NE < CH < PHDMS. The dielectric loss angle increased in the RF field up to a maximum value that corresponds to a critical frequency. The addition of additives to the plastisol PVC blend, as mono, binary, ternary or quaternary mixture, has a beneficial effect upon the dielectric behaviour of final films, making them suitable for use in the footwear manufacturing.*

Key words: *leather substitutes, polymer films, plasticizers, radio frequency field, dielectric relaxation*

1. INTRODUCTION

PVC is increasingly used as a substitute for leather, because it is cheaper and offers great flexibility to fashion designers, without raising the environmental or ethical issues sometimes associated with genuine leather.

For plastified PVC films, specialty literature mentions many research works on dielectric properties in which the dependence between dielectric permittivity ϵ_r or loss factor and frequency is presented, but no reference to multicomponent formulations was found [1-4]. Some of the common factors that influence the dielectric strength of a material are: temperature, humidity, material thickness frequency of applied voltage. It is known that an increase in the frequency will result in increased dielectric strength or breakdown voltage [3, 4].



When an insulating material is subjected to alternating voltage, some of the electrical energy is absorbed by the insulating material and this energy is dissipated as heat. This amount of energy absorbed by the material is called dielectric loss [5-8].

In the case of a perfect dielectric material, current leads the voltage by 90 degrees but this is not the case with practically available dielectric materials. In practical case it is less than 90 degrees, say it an angle Θ . The $(90-\Theta)$ difference is called dielectric loss angle, $\text{tg } \delta$ and is a very important property of insulating materials. The addition of different additives to the PVC-based mixture can significantly change their dielectric properties. As above mentioned, the best dielectric properties are exhibited by binary, ternary, and/or quaternary blends, from which plastified PVC films were obtained through a methodology described in [6-10]. In respect to monocompound products, dielectric properties were studied in order to find any possible synergetic or anergetic effects in binary, ternary or quaternary blends.

It is the aim of this paper to investigate the influence of chemical auxiliaries/additives and the RF field frequency upon the dielectric behaviour of plastified PVC films intended for leather substitutes with uses in the footwear industry, for the manufacture of shoe uppers.

2. MATERIALS AND EQUIPMENT

The components of the basic recipe are: Polyvinyl chloride, PVC (Sigma Aldrich), with the following chemical and physical characteristics: molecular weight $M = 4000$ g/mol, viscosity index $K_{\text{wert}} = 65-67$, density $0.48-0.56$ (powder PVC emulsion type); Dioctylphthalate, DOP (Limited England), with a viscosity of $74-76$ cP and $M = 390$ g/mol; thermal stabilizer of Cd-Zn type KZII (România); blowing agent Genitron AC₄, BA (Limited England). The chemical auxiliaries used in the recipe formulation were: polydimethylsiloxane, PDMS (Sigma Aldrich) with $M = 17537$ g/mol; polymethylhydrosiloxane, PHDMS (Sigma Aldrich) with $M = 16180$ g/mol; nonylphenol ethoxylate emulsifier emulsifier NF10, NE (România); collagen hydrolizate, CH with $M = 30000$ g/mol and $\text{pH}_{\text{iz}} = 10.8$ (România). The auxiliary agents were added as mono, binary, ternary or quaternary mixtures. The following laboratory equipment was used: Werner Mathis type LTE-S-B apparatus for film forming; laboratory Roll Mill Type W 110 E for mixture preparation; gelling vacuum oven type Horyzont (Germany).

The high frequency electric field for treatment of PVC plasticized films was provided by a high frequency capacitive generator with 380 V supply voltage, and 13.56 MHz working frequency. Temperature was controlled by a non-contact infrared (IR) thermal sensor. The dielectric loss angle was measured with a Q-meter type LCR-Q (Model HP4284), with variable capacity, in the range 50 KHz-14.8 MHz [11-13].

3. EXPERIMENTAL

Mixtures for the preparation of plasticized PVC films were obtained accordingly with the following recipe: PVC (polyvinyl chloride) -100 parts, DOP (dioctylphthalate)- 60 parts, thermal stabilizer (KZ II)- 3 parts, blowing agent(BA) (Genitron AC₄) – 2 parts, auxiliary agents (CH-collagen hydrolizate, polydimethylsiloxane (PDMS), polydimethylhydroxisiloxane (PHDMS), Nonionic emulgator type NF10 (NE): 4 - 6 parts.

Plastisol mixtures were prepared from the above-mentioned constituents on the mixing roll mill and degassed for 15 min. in a vacuum oven at 30°C.

Films of 0.5 mm thickness were formed on a teflon antiadherent plate in the Werner Mahis apparatus, and pregellified for 20 s at 120°C in RF field, at 13.56 MHz working frequency. The subsequent blowing/expanding operation was performed at 190 °C at the same working frequency.

Treatment time ranged between 30 and 120 seconds. Rectangular (20×100 mm) and circular (60 mm diameter) test specimens were cut from the PVC films. Experimental determinations were made on representative PVC films (containing mono, binary, ternary and quaternary mixture of chemical additives) in order to determine the dependence of $\text{tg } \delta$ on the frequency of the RF field. The variable frequency was achieved on the Q-meter, and $\text{tg } \delta$ was measured by the resonance method on a capacitive oscillating circuit [12-16].

4. RESULTS AND DISCUSSIONS

Experimental data presented in fig. 1-7 show that polarisation of studied chemical auxiliaries/additives is function of external field frequency and dielectric nature of the compound, (BA is the blowing agent and additives in mixture are generally denoted by AM). Thus, the $0.5 \cdot 10^5 \div 7 \cdot 10^5$ Hz frequency range leads to a partial orientation of the voluminous, high molecular weight structural elements of the compound, indicating some polarization and oscillatory displacement. The internal (rotational) friction is prevailing. At the same time, a maximum orientation of low volume structural elements (free radicals reactive groups, chain ends) is noticed, which are subjected to rapid oscillatory motion in the $7 \cdot 10^5 \div 1.48 \cdot 10^7$ Hz frequency range.

In these situations, two domains can be distinguished:

- in the first case, the “dipole-elastic” loss domain, in which a maximum value, α of the dielectric constant, ϵ' is observed, due to the polarisation in alternative electric field of COO^- , -NH_2 , -OH groups present in auxiliaries such as: polyhydroxymethylsiloxane (PHDMS), collagen hydrolyzate (CH), or non-ionic emulsifier (NE).

- in the second case, the “dipole-radical” loss, in the high frequency domain; the maximum, β of the dielectric constant, ϵ' , caused by the displacement of nonpolar radicals, can be noticed.

So these phenomena are due to dielectric relaxation of both polar and non-polar mobile radicals.

The evolution of the measured dielectric loss vs. compounds nature and concentration present a behaviour that is characteristic to polar polymers, like PVC, CH, PDMS and PHDMS.

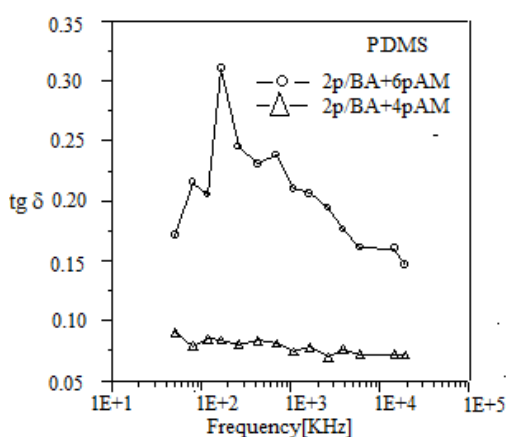


Fig.1. The dependence of $\text{tg } \delta$ on the RF field frequency, for the PDMS-containing mixture

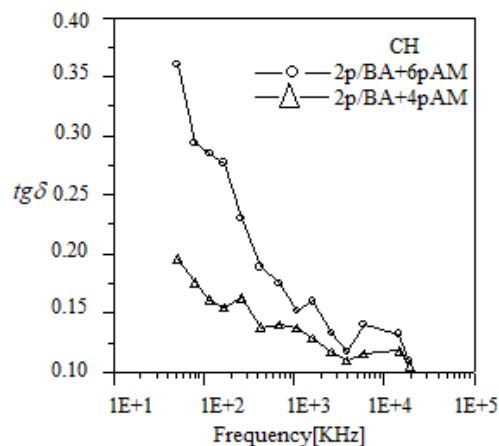


Fig.2. The dependence of $\text{tg } \delta$ on the RF field frequency, for the CH-containing mixture

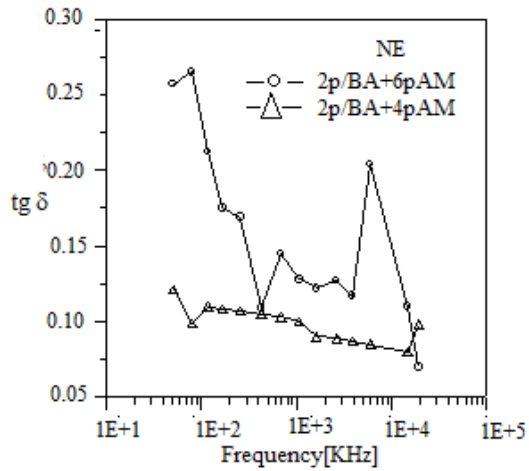


Fig. 3. The dependence of $tg \delta$ on the RF field frequency, for the NE-containing mixture

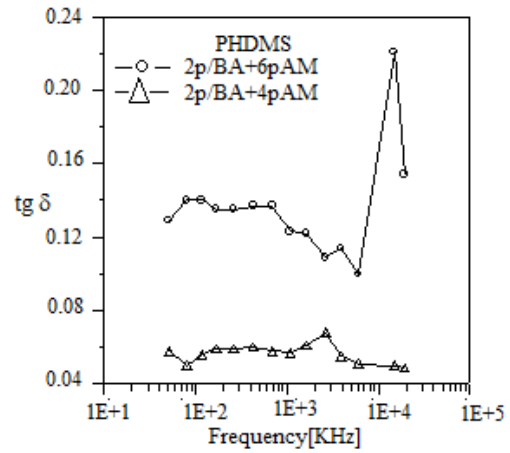


Fig. 4. The dependence of $tg \delta$ on the RF field frequency, for the PHDMS-containing mixture

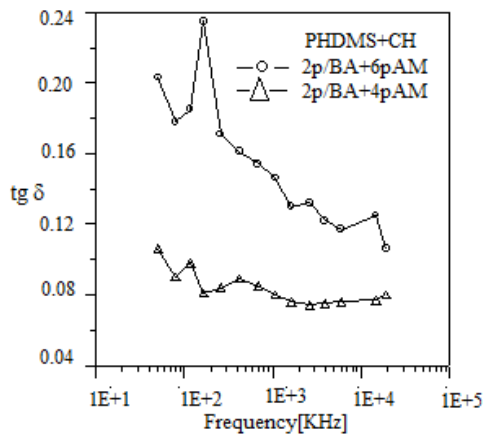


Fig. 5. The dependence of $tg \delta$ on the RF field frequency, for the (PHDMS+CH)-containing mixture

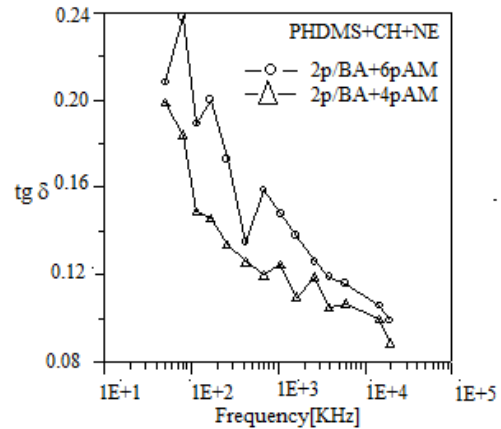


Fig. 6. The dependence of $tg \delta$ on the RF field frequency, for the (PHDMS+CH+NE)-containing mixture

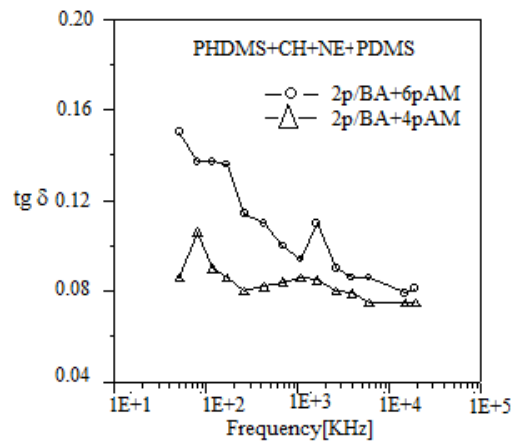


Fig. 7. The dependence of $tg \delta$ on the RF field frequency, for the (PHDMS+CH+NE+PDMS)-containing mixture



The analysis of experimental data presenting the variation of loss factor vs. frequency (shown in figures 1-7) allows the following findings:

- The blends containing 4 parts auxiliaries show lower loss factor values in comparison with blends containing 6 parts of chemical auxiliaries;
- Both type α and β relaxation were observed;
- It is apparent that the relaxation time is defined as the time in which the polymeric compounds from the studied blend will re-establish a new equilibrium state, or make new displacements.

It must be noticed that for a certain value of the external field frequency, termed as critical frequency, a high energy absorption occurs, due to resonance between the self- frequency of the polar group and external field frequency. The critical frequency is pointed out by the higher peak on the frequency – $\text{tg } \delta$ diagrams.

For all studied blend, low frequency values lead to high dielectric loss angles, which decrease when frequency is increased. The oscillations of dielectric measures are due to conduction processes that take place due to the existence of free charge carriers (side group such as OH, CH₂, NH₂, Cl, etc), which at the beginning of the process are in phase with the external current and lead to the increase of dielectric loss. At the same time, the “dipole-elastic” domain is prevailing at frequency lower than 10⁵Hz, and the type α relaxation occur. The first characteristic peak is observed in this low frequency range.

In the high frequency range (more than 10⁶Hz), “dipole-radical” loss occur, which are characteristic to the β maximum of dielectric constant, ϵ' (β type dielectric relaxation). The “dipole-radical” loss is more obvious in blends containing nonionic emulsifier and polysiloxane auxiliary, respectively. Multi-component blends show many characteristic peaks, determined both by the chemical nature of components and the interaction between them. At high frequency, peaks characteristic to “dipole radical” loss (β type) are alleviated in ternary and quaternary blends in comparison with individual components, thus indicating some anenergetic effects.

The fact that ternary and/or binary blends present best behaviour in high frequency electric field can't be explained only by means of dielectric properties. All factors involved in the manufacturing process of the porous sheet structures must be taken in account.

5. CONCLUSIONS

Study of the behaviour of plastified PVC films exposed to external high frequency field under laboratory experimental conditions led to the following conclusions:

1. The addition of different chemical auxiliaries in the plastisol PVC blends determines changes in dielectric loss of resulting films. Thus, the increase of auxiliaries concentration determines the increase of the dielectric loss up to a maximum value irrespective the nature of the chemical auxiliary, indicating a satisfactory behaviour in high frequency electric field; consequently, high values of dielectric loss will be favorable to structures obtained;

2. The dielectric loss of PVC films, imparted by the presence of chemical additives, increased in the following order: PDMS < NE < CH < PHDMS;

3. The dielectric loss is in direct dependence with the additive concentration. In all cases, blends containing 4 parts auxiliaries presented lower loss factor values in comparison with those containing 6 parts auxiliaries;

4. Variation of dielectric loss vs. external field frequency in the studied films indicate a specific behaviour, determined by the nature and concentration of components. At a certain value of the external field frequency named “critical frequency” an increased absorption energy is noticed



due to the resonance between the self-frequency of polar groups and the external field frequency, as proved by more pronounced peaks.

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