THE INFLUENCE OF TEMPERATURE AND RECIPE FORMULATION ON THE DIELECTRIC BEHAVIOUR OF PLASTIFIED PVC FILMS

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Abstract: Radio frequency fields (RF fields) have well-established uses in the manufacturing industries, as environmentally friendly heat sources. Synthetic polymer films can benefit from RF fields in several operations of the processing train, like gelification and blowing. Plastified polyvinyl chloride (PVC) films are some of the most popular products of this kind and have different applications in consumer goods, like clothing and footwear. Films properties depends on the recipe of the plastisol blend and on the processing parameters. This paper presents the combined influence of temperature and the nature of some auxiliaries, added to the plastisol blend, upon dielectric characteristics of plastified PVC films, obtained in high electric frequency field. The chemicals used as additives in the recipe formulation were: polydimethylsiloxane (PDMS) polymethylhydrosiloxane (PHDMS), nonylphenol ethoxylate emulsifier NF10 (NE) and collagen hydrolizate (CH). The RF field was provided by a high capacitive generator with 380 V supply voltage, and 13.56 MHz working frequency. Variation of dielectric loss angle, tg δ and dielectric permittivity, ε_r' were recorded over a temperature range of 20°C-160°C, in the frequency range 50 KHz-14.8 MHz. The phenomena of polarization, appeared in RF field, are either dipole - elastic or dipole-radical type. Attainment of resonance frequency determines an accelerated "internal friction" that produces heat, which causes the thermal decomposition of the blowing agent and the emergence of the porous structure. The losses factor presents a significant increase, passes through a maximum, and decreases with temperature, except the ternary mixture. For all the studied mixtures, a slight increase of ε_r' at temperatures above 110°C was noticed.

Key words: unconventional heating, radio frequency field, polymer film, polymer dielectrics, leather substitutes

1. INTRODUCTION

Specialty literature and research carried out in the last decades emphasize the advantages of using the radio-frequency fields (RF fields) in different areas of activity, like machinery manufacturing, agriculture, pharmaceutical and plastics industries [1-3], clothing and leather industry, bioengineering, etc. [4-6]. In the production of leather substitutes, the use of high frequency field is relatively recent, mainly for the obtaining of different porous material for the lower parts of footwear, like heels and soles [7]. Recent international and national research confirmed once again the advantages of this unconventional treatment technique, as compared with the conventional ones, for the obtaining of synthetic polymer films [8]: increased efficiency (63%), as compared with 32-34% for the classical heating techniques; higher productivity; lower utilities

(water, steam, and electric energy) consumption; reduced number of maintenance personnel; reduced treatment time (by 3-4 times shorter than those of conventional procedures); the possibility of performing different operations involving heat transfer and change of material structure on the same machine: gelification, foaming, grafting, polymerization, cross-linking, drying, dyeing, impregnation, etc.[9].

In accordance with the electromagnetic field theory applied to a dielectric material, the result of the material-field interaction, at macroscopic level, is a perceivable heating of the material. In fact, heat generation is produced due to some simultaneous phenomena, like dipole rotation, ionic conduction, interface polarization, dipole elongation, dipolar electric resonance, etc. From all of these, the preponderant for the observed processes is that of ionic conduction, and especially that of dipolar rotation and dielectric resonance. These phenomena are more or less strongly manifested, depending on the chemical structure of the material constituents [10]. As presented in previous articles, [11, 12] the addition of certain chemical auxiliaries to the recipe of plastified PVC films, can significantly improve the physical-mechanical and hygienic properties of the expanded films. It is difficult to establish the predominant phenomenon from those previously mentioned, because these components are not separated in the studied mixtures, but they evolve in continuous interaction until the end of thermic processes which take place under the action of the extern electric field [13]. In this context, it is the aim of this paper to study the effect of plastisol blend formulation and temperature upon some dielectric characteristics of plastified PVC films; *in accordance with the REACH Regulation (EC 1907/2006) wich imposes some restrictions on the use of certain chemicals (such as nonylphenol ethoxylate or dioctylphtalate in the blend formulations), the resulting PVC films can be used to obtain products that are not subject to washing cycles or do not come in direct contact with the body, such as artificial leather for shoe upper or some leather goods [14].*

2. MATERIALS AND EQUIPMENT

The constituents 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 Kwert = 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). 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 pH_{iz}=10.8 (România). The auxiliary agents were added as mono, binary, ternary or quaternary mixtures. The following laboratory equipment was used: laboratory Roll Mill Type W 110 E for mixture preparation; Werner Mathis type LTE-S-B apparatus for film forming; vaccum oven type Horyzont (Germany) for films gelification.

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.

3. EXPERIMENTAL

Mixtures for the preparation of plasticized PVC films were obtained accordingly with the following recipe: PVC (polyvinyl chloride) - 100 parts, DOP (dioctylphtalate) - 60 parts, thermal

stabilizer (KZ II) - 3 parts, auxiliary agents (CH-collagen hydrolizate, polydimethylsiloxane (PDMS), polydimethylhydroxisiloxane (PHDMS), Nonionic emulgator type NF10 (NE): 4 - 6 parts.

The plasticized PVC films samples tested in this study were as follows:

1. Control sample, prepared only with the constituents of the basic recipe (PVC, plasticizer, blowing agent, thermal stabilizer) ;

2. Samples prepared by the addition of a binary mixture of CH + PDMS;

3. Samples prepared by the addition of a ternary mixture of PDMHS + CH + NE;

4. Samples prepared by the addition of a quaternary mixture of PDMHS+HC+NE+PDMS.

At laboratory scale, the plastified PVC films were obtained as follows: a homogenous blend was firstly prepared in accordance with the basic recipe, by thoroughly mixing in a mortar and pestle the PVC powder, the plasticizer, and the thermal stabilizer. Recipes containing auxiliaries were prepared from portions of the basic recipes, by adding the corresponding binary, ternary and quaternary mixtures. The resulting blends were then homogenized and deaerated on the roll mill. Films of 0.5 mm thickness were drawn on a Teflon antiadherente plate in the Werner Mahis apparatus. The films thus obtained were pre-gelified at 120°C for 4 min and gelified at 130 ºC -160 ºC for 2-3 min. Both pre-gelification and gelification were performed in RF field, at 13.56 MHz working frequency; during gelification, temperature values were recorded with the IR pyrometer.

Rectangular (20×100 mm) and circular (60 mm diameter) test specimens were cut from the PVC films for measuring dielectric properties. Experimental determinations were made on representative samples (containing mono, binary, ternary and quaternary mixture of chemical additives) in order to determine the dependence of dielectric loss angle (or loss factor), tg δ and dielectric permittivity, ε_r' on temperature. Variation of loss factor was recorded over a temperature range of 20°C-160°C, with a variable capacity Q-meter, type LCR-Q meter (Model HP4284), in the frequency range 50 KHz-14.8 MHz, using the resonance method on an oscillate capacitive circuit, in accordance with a methodology described in other works [15-17].

4. RESULTS AND DISCUSSIONS

The fluid components with polar structure exhibit an increased freedom of movement under the external electric field action; the higher the frequency of the external field, the higher tendency for dipole orientation. On the other side, under the high frequency field action, this mobility that induces a so-called supplementary internal plastifying, which contributes to the reduction of the loss factor, is counteracted by the interaction between the mixture constituents. Among unreacted remnants of the auxiliary and blowing agents free radicals or interactions (because of the vibration frequency in resonance with the extern electric field) may appear, which result in the increase of losses factor value of the dielectric material, up to a value that corresponds to a critical current intensity, termed as breakdown current.

Even if initially the material contained components whose concentration corresponded to the domain of optimal dielectric losses, an amplification of vibration frequency of the dipoles from the mixture took place, (because of electric resonance phenomena), that determined an accelerated dielectric loss increase till dielectric breakdown, due to the formation of an electric arc that brought out the installation from the circuit [18, 19]. This phenomena can be counteracted either through the control of the geometrical factors (the geometry of the condenser fitting in the case of the high frequency field) or through the control of the intensity of the applied electric field, introducing IR pyrometer into the circuit. Beside the above mentioned phenomena, another one can be noticed: due to lower relaxation frequency of some of the mixture constituents (like collagen hydrolyzate, polysiloxanes, polyvinylchloride) as compared with the frequency of the external electric field, rapid

growth of the material temperature takes place; this can be explained by the emergence of the resonance frequency in the mixture molecules, which determines an accelerated "internal friction" having as a final result a significant heating of the material. Finally, this heating will cause the thermal decomposition of the blowing agent and hence the apparition of the porous structure, or only gelification and consolidation of the film in the absence of the blowing agent.

During the films treatment in the RF field, rapid shifting of the component dipoles from the mixture are produced, which have the following effects: structural transitions from an ordered form to another one; local movement of side groups or free radicals ($-NH_2$, $-COOH$, $-OH$, $-CH_3$ etc.) similar to Brownian movement, which is reflected in a change of the dielectric permittivity, ε'_r and of the loses factor, $tg\delta$ values.

From the examination of the dielectric spectra (fig.1-4), which presents the variation of $tg\delta$ and ε'_r with temperature, the following comments can be made:
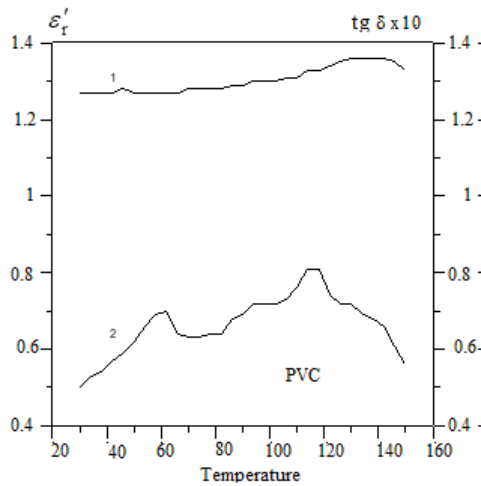

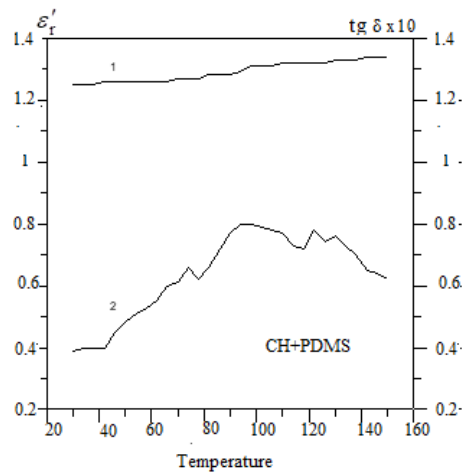**Fig. 1.** *The variation of ε'_r (1) and tg δ (2) with temperature for PVC film (control sample)*

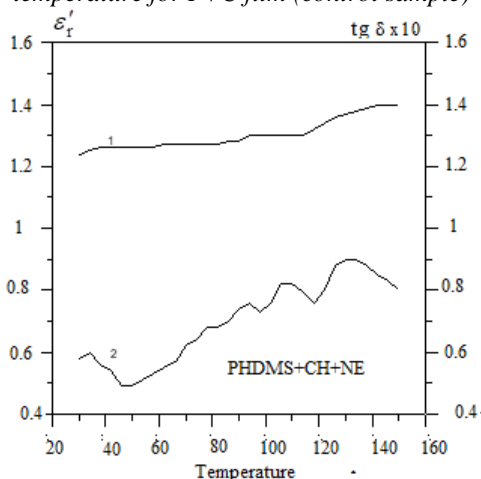**Fig. 2.** *The variation of ε'_r (1) and tg δ (2) with temperature for the (CH+PDMS) mixture*

Fig. 3. *The variation of ε'_r (1) and tg δ (2) with temperature for the (PHDMS+CH+NE) mixture*
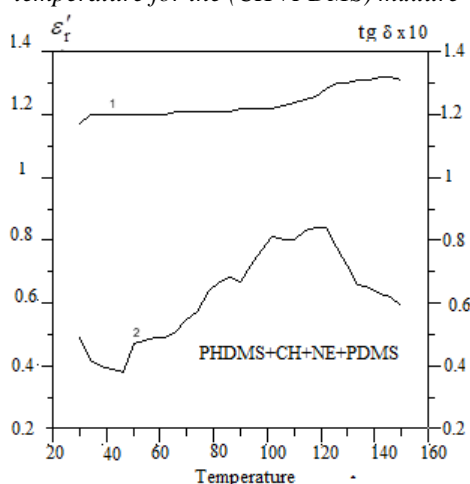

Fig. 4. *The variation of ε'_r (1) and tg δ (2) with temperature for the (PHDMS+CH+NE+PDMS) mixture*

For all the studied mixtures, a slight increase of the dielectric permitivity, ε'_r at temperatures above 110ºC can be noticed, which is characteristic for the dielectrics with attenuated relaxation phenomena. The losses factor (tgδ) presents a significant increase with temperature rising, passes through a maximum, and decreases with temperature increase, except the ternary mixture. On the variation curves of the losses angle tangent and of the dielectric constant by the temperature, the relaxation state τ_c (the characteristic relaxation time) corresponds to the inflexion point on the ε'_r curve and to the maximum on the tgδ curve. Depending on the mixture composition, the tgδ variation with temperature presents characteristic peaks, which correspond to a relaxation processes with different kind of molecular mechanism. In the case of the control sample, two characteristic peaks can be observed, which correspond to some relaxing processes with molecular mechanisms of different nature. The presence of a peak at 110^0C can be noticed, which corresponds to the α type relaxation (around the vitreous transition) and another peak at the 60^0C, corresponding to β type relaxation (determined by damping of oscillation of the chain ramification around the equilibrium point).

Because of the mixtures complexity and the polar character of most of them, the existence of more dipole types must be taken in consideration, each one with its own characteristic relaxation time, which determines the apparition of peaks in the dielectric relaxation spectrum of studied films.

In the case of binary mixture, a shifting of α transition to a lower temperature occurs, which indicates a plasticizing effect mainly due to the alkyl radical from the polysiloxane component, which slows down the intermolecular relaxation. For the other mixture, the chain mobility decreases, because of the new polar groups introduced in PVC base mixture and the increase of macromolecular interaction; consequently, the α transition is shifting to higher temperature. This effect is most obvious in the ternary mixture. For all mixtures an attenuation of the peak can be noticed, which is characteristic to β transition compared to the control sample, with more obvious shifting to higher values, in the case of ternary mixture, too.

5. CONCLUSIONS

The obtaining of plastified PVC-based films with improved dielectric characteristics is significantly favoured by the addition of auxiliaries such as hydrolyzed collagen, siloxane polymers (polydimethylsiloxane, polydimethylhydroxysiloxane), or non-ionic emulsifiers to the plastisol recipe.

The binary mixture shows a shifting of α transition to a lower temperature which indicates a plasticizing effect mainly due to the alkyl radical from the polysiloxane component, which slows down the intermolecular relaxation, while in the ternary mixture the α transition is shifting to higher temperature due to the increase of macromolecular interaction.

With the variation of the temperature the apparition of α or β types relaxation phenomena, characteristic to the dipole-elastic or dipole-radical losses can be noticed.

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