

NOTE

Effect of Plasticizer Nature and Content on the PVC Stability and Dielectric Properties

H. DJIDJELLI,¹ T. SADOUN,¹ D. BENACHOUR²

¹ Laboratory of Organic Materials, Chemical Processing Institute, University of Bejaia 06000, Algeria

² Chemical Processing Institute, University of Setif, 019000, Algeria

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INTRODUCTION

Polyvinyl chloride (PVC) has a large sales volume, second only to polyethylene. Its high chlorine content provides it with a very high level of combustion resistance for building products, electrical enclosures, and wire and cable insulation. PVC has a unique ability to be compounded with a wide variety of additives, making it possible to produce materials in a range from flexible elastomers to rigid compounds. In service, cracking cable may result from thermal expansion and contraction or from insulating material shrinkage with aging.

The electrical analysis is one of the techniques most frequently used to characterize and study the degradation of polymers. Several studies can be found in the literature where the dielectric properties of some mixtures of polymers are studied. Hanna et al.^{1,2} studied the dielectric behavior of neoprene mixed with carbon black, over a wide frequency and temperature ranges. Tang et al.³ studied the effect of processing conditions on the electrical and dynamical behavior of carbon black filled ethylene/ethylacrylate copolymers. The physico-mechanical and dielectric properties of styrene butadiene rubber mixed with Kaolin have been studied at different temperatures and frequencies by Aziz et al.⁴ The effect of plasticizer on the decomposition of PVC is a complex phenom-

non that is still not well understood and the results and conclusions obtained by different authors may be markedly different. Wypych⁵ found that the plasticizer can be included in either of the two following groups: dioctyl phthalate, dioctylazelate, diisooctyl adipate, which increase the thermal stability of the polymer and butylbenzyl phthalate, diphenyl octyl phosphate, and tricresyl phosphate, which decrease the stability of the polymer. Minsker et al.⁶ observed that the rate of PVC degradation increased when using plasticizers of the alkyl and alkyl-aryl type. On the contrary, Kovacic et al.⁷ obtained results very different than those obtained by Minsker. Marcilla and Beltran^{8,9} found that the presence of the dioctyl phthalate (DOP) accelerates the process of decomposition of PVC. Millan et al.¹⁰ showed that the mixture of PVC with an incompatible polymer does not affect its stability. Nevertheless, the mixture with a compatible highly rigid polymer hinders the movement of the GTTG-conformations in the PVC, resulting in a stabilizing effect. In the present study, the effect of concentration of two type of plasticizers and their blend on the properties of PVC were investigated by a determination of the following: mass loss by thermogravimetry, dielectric rigidity, and dielectric loss factor.

EXPERIMENTAL

Materials

PVC, suspension grade (PVC 4000 M, Product of Algeria ENPC, $K = 65$ to 67 , density = $0.48-$

Correspondence to: H. Djidjelli. E-mail: hocine_djidjelli@hotmail.com

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0.567) was used in this investigation. Barium-cadmium was used as stabilizer, lead stearate was used as a processing aid (lubricant) and DOP, diisodecyl phthalate (DIDP), and a blend of [DOP-DIDP (1:1)] as plasticizers.

Preparation of Formulations

Mixtures of PVC with 1 phr of lubricant, 2 phr of stabilizer, and different ratio of each plasticizer, were prepared and noted by:

The formulations plasticized by DOP 10, 20, 30, 40, and 50 phr were noted by M10(DOP), M20(DOP), M30(DOP), M40(DOP), and M50(DOP) respectively.

The formulations plasticized by DIDP 10, 20, 30, 40, and 50 phr were noted by M10(DIDP), M20(DIDP), M30(DIDP), M40(DIDP), and M50(DIDP) respectively.

The formulations plasticized by blend of (DOP-DIDP) 10, 20, 30, 40, and 50 phr were noted by M10b, M20b, M30b, M40b, and M50b respectively.

No plasticized formulation was noted by M0.

The dry blends were obtained using a mixer at 50°C and at 3000 tr/min rotational speed. The mixed compounds were molded in the form of 2-mm-thick sheets in a compression molding machine. The molding was performed at 180°C and 300 bars for 15 min. After molding, the samples were cut from the molded sheet electrical and thermal studies.

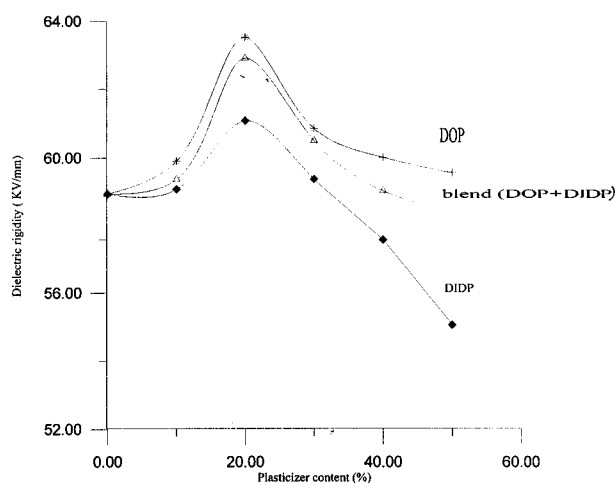


Figure 1 Effect of plasticizer nature and content on the dielectric rigidity.

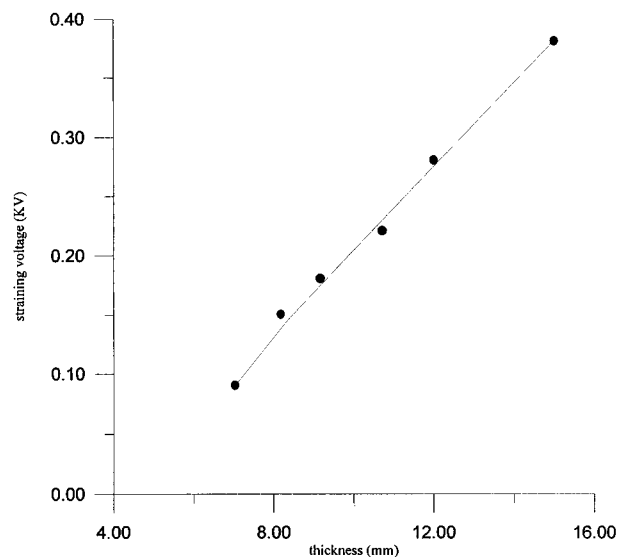


Figure 2 Effect of sample thickness on the straining voltage for the M40(DOP) formulation.

The dielectric rigidity test was determined using an Apparatus IPE3 and the dielectric loss factor was determined using a Schering bridge Tetex AG 2809a. The voltage and frequency applied were 100 V and 50 Hz. The experiments for determination of a mass loss were performed using a SETARAM TGT thermobalance model DTA-92 controlled by an EPSON compatible system. The atmosphere used was nitrogen. Samples of approximately 4.5–5.0 mg were placed in the platinum crucible of the thermobalance. The experiments were performed to the final temperature of 600°C at 10°C/min.

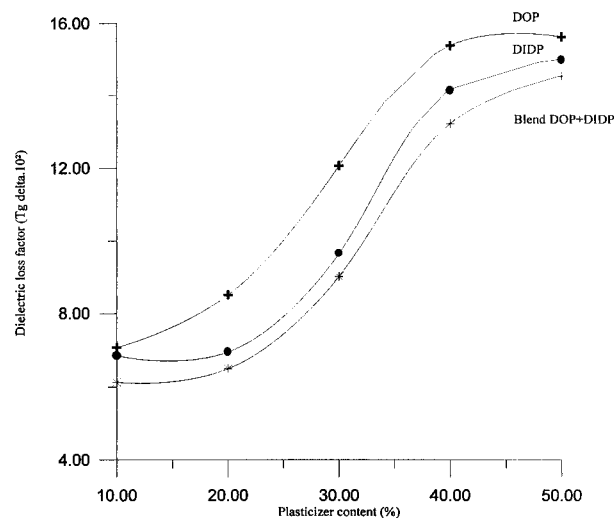


Figure 3 Dielectric loss factor as function plasticizer content for different plasticizers, measured at 80°C.

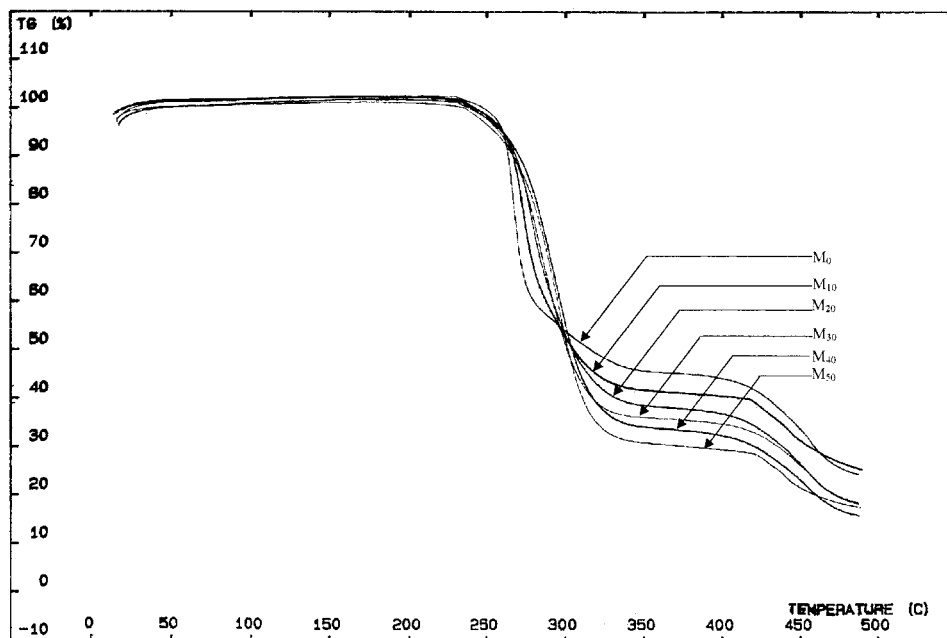


Figure 4 Thermograms of different samples as a function of DOP content.

RESULTS AND DISCUSSION

Influence of the Plasticizer Nature and Content on the Dielectric Rigidity

Figure 1 shows clearly the effect of plasticizer nature and content on the PVC dielectric rigidity (defined as the tension needed to induce the ma-

terial perforation). We noticed an increase of the dielectric rigidity in the 0–20 phr interval (with respect to the content) for all samples. Beyond that, a decrease in the dielectric rigidity was observed. Such a decrease may be attributed to the increase in the conductivity and mobility of chain segments. Thus, the plasticizer creates defects

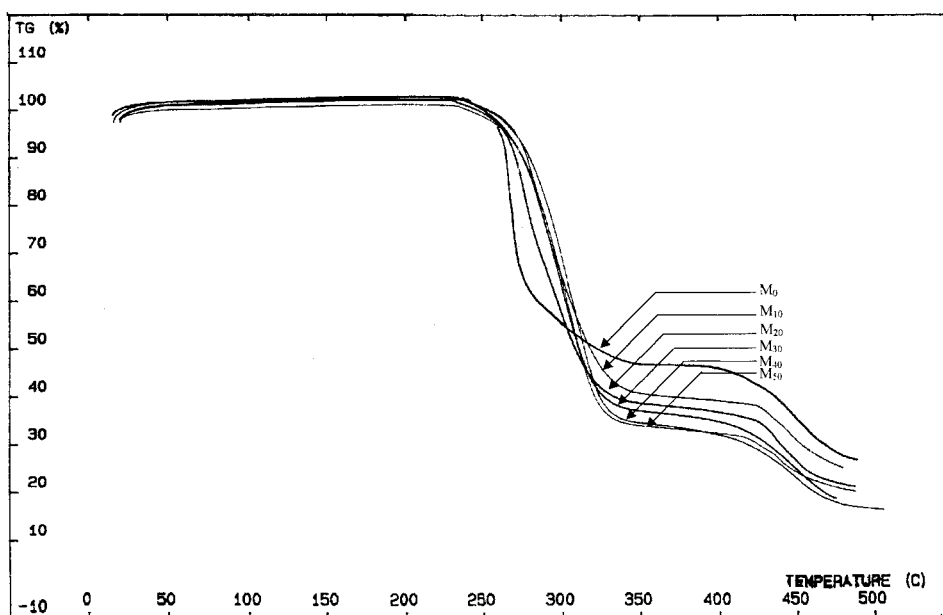


Figure 5 Thermograms of different samples as a function of DIDP content.

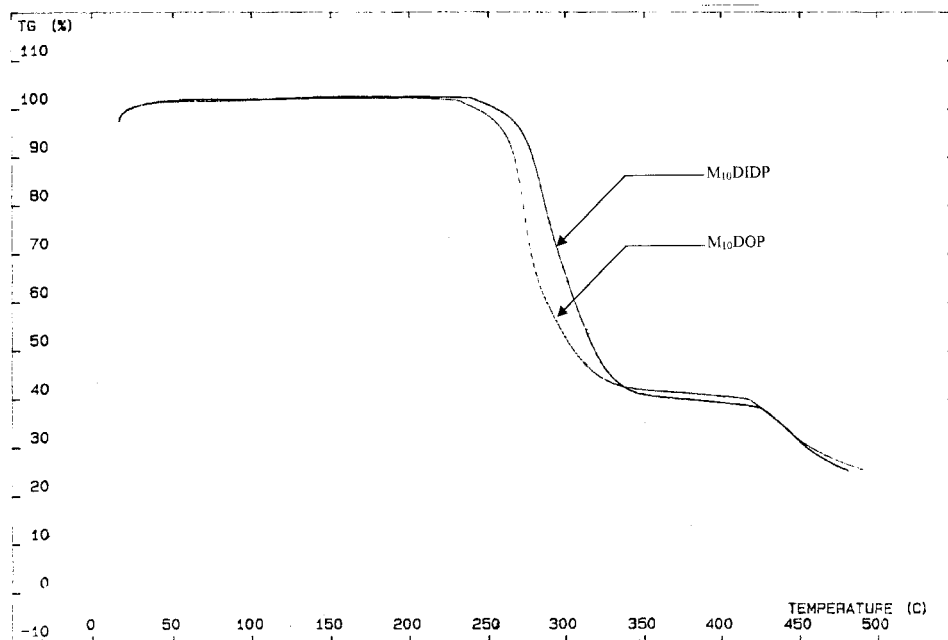


Figure 6 Thermograms of different samples, at 10% plasticizer content, as a function of plasticizer nature.

within the dielectric material. Results comparison indicates that samples plasticized with DOP present a better rigidity than those plasticized with DIDP as well as those plasticized with the DOP–DIDP blend. This may be attributed to the alkyl radical of the plasticizer: that of the DIDP is longer than that of the DOP.

Effect of Sample Thickness on the Dielectric Rigidity

Figure 2 shows an increase in the straining voltage (E_s) with an increase in sample thickness (e , mm). The measures of straining voltage of the different samples of different thickness were done

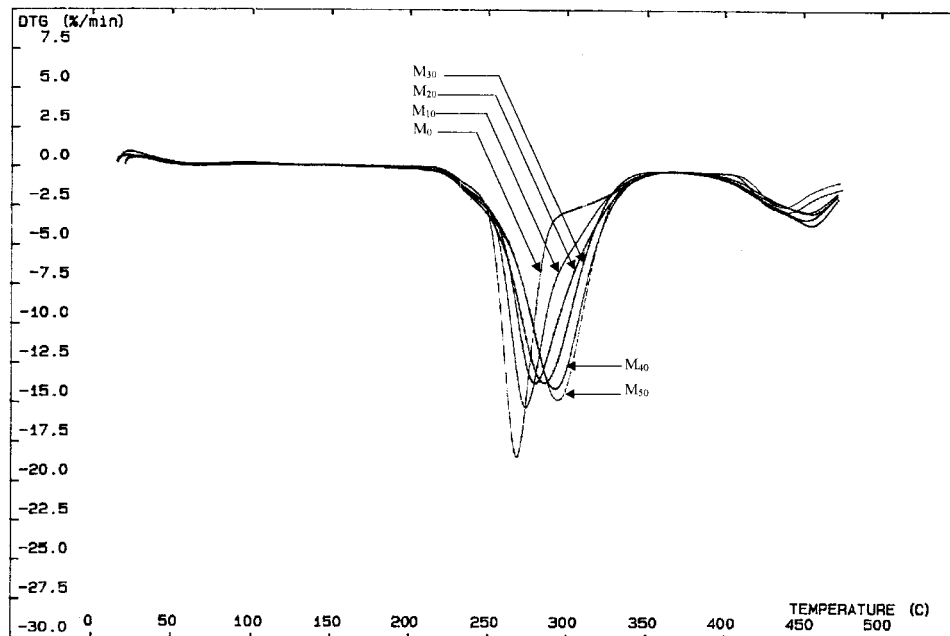


Figure 7 Thermal degradation rate as a function of DOP plasticizer content.

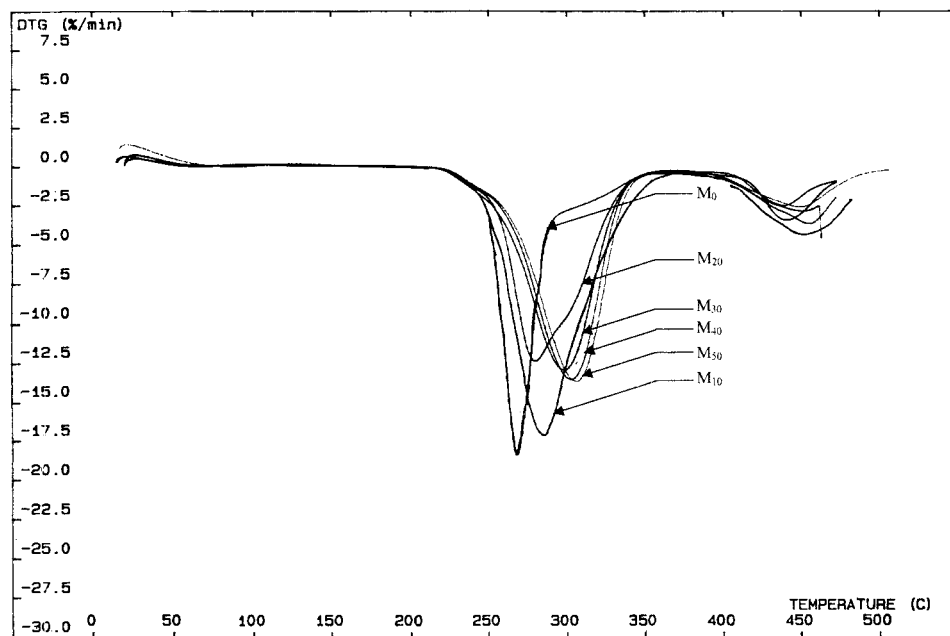


Figure 8 Thermal degradation rate as a function of DIDP plasticizer content.

on the samples plasticized at 40 phr. The measures of straining voltage of a film are calculated on the base of average of five acceptable measures statistically on the same sample. The draw of the curved straining voltage in function of the thickness given a straight line equation:

$$E_s = 23.92 t + 4.98$$

where E_s is straining voltage of the sample (KV) and t is the thickness (mm)

This equation allows us to make the appropriate choice of the sample thickness according to the final use of the compound.

Influence of Plasticizer Nature and Content on the Dielectric Losses ($\tan \delta$)

Figure 3 shows that the use of a plasticizer, whatever its nature and its content, will increase the dielectric losses of the PVC (decrease in the insulating properties). This phenomenon may be explained by the fact that the plasticizer is a polar molecule with a nucleophilic character. Its introduction within the PVC matrix increases the polarity by creating electric dipoles that will result in a reduced insulation. Often the material (PVC) is plasticized, thus changing it from brittle to a tough and flexible material. Plasticizing has a big effect on the dielectric properties, because it shifts

the glass transition to lower temperature.¹¹ The value of the dielectric loss factor for PVC rigid is in the range 0.007 to 0.01.

Experiments have also shown that dielectric losses increase with the increase of plasticizer content and reach a maximal value at about 40 phr plasticizer content.

We noticed also that the use of a plasticizer blend of DOP and DIDP gave a synergetic effect, i.e, samples obtained with the plasticizer blend presented less dielectric losses.

Sample Mass Loss Determined by Thermogravimetry

Figures 4 and 5 illustrate the effect of plasticizer nature and content on the sample mass loss. The curves have similar shape for all formulations and each one presents two distinct stability

Table I T_{\max} as Function of DOP Content

DOP (%)	T_{\max}
0	268.3
10	273.83
20	278.26
30	288.04
40	293.48
50	296.73

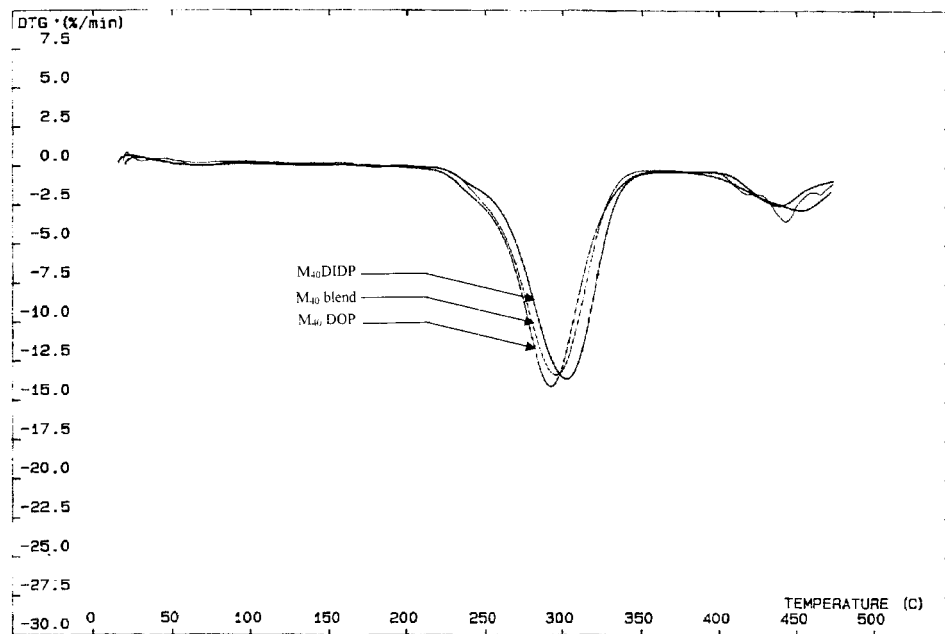


Figure 9 Thermal degradation rate as a function of temperature for different plasticizers.

stages. Mass loss starts at 200–210°C and accelerates sharply at 250°C when the sample has lost about 50% of its initial mass. Upon heating over 500°C, the remaining residue stays stable more or less.

The first stage corresponds to the plasticizer migration and the step-by-step elimination of HCl with some benzene traces. The second stage corresponds to polyacetylene formation that gradually reticulates and becomes more stable than PVC. From 400°C, a mass loss is observed and is attributed to the polyacetylene cracking. Thermogram comparison allowed us to conclude that mass loss is more important in the case of samples less plasticized, at temperatures below 300°C. This phenomenon may be explained by the fact that the plasticizer slows down the sample degradation, i.e., the plasticizer has the advantage to ameliorate the stabilizer distribution within the polymer. As an example, at equal temperature of 275°C, the registered mass loss is: M0 = 34.14%, M10(DOP) = 28.57%; M20(DOP) = 20%, M30(DOP) = 17.86%, and M50(DOP) = 15.36%.

Starting from 300°C, we obtained polyacetylene formation. The phenomenon observed initially was reversed, i.e., mass loss was lower for the less plasticized samples. This may be attributed to the polyacetylene reticulation that starts around such a temperature. For instance, at

equal temperature of 350°C the registered mass losses are as follows: M0 = 51.79%, M10(DOP) = 57.86%; M20(DOP) = 61.43%, M30(DOP) = 65.00%, M40(DOP) = 66.43%, and M50(DOP) = 70%.

On the other hand, Figure 6 shows clearly the difference between formulations plasticized with DOP and those plasticized with DIDP. We note that the mass loss is more important for the DOP formulations for temperatures below 350°C. This is due to the difference in the volatility temperature, the difference explained by the molecular weight difference between the two plasticizers ($M_{\text{DOP}} = 390$ g/mol and $M_{\text{DIDP}} = 446$ g/mol).

Mass Loss Rate of the Different Formulations (DTG)

Figures 7 and 8 illustrate the mass loss rate as a function of temperature for the different samples. It may be noted that the plasticizer retards degradation, i.e., the less plasticized samples degrade faster. This is attributed to the inhibition reaction of HCl production induced by the plasticizer and the solvation by the plasticizer ester groups of the labile chlorine which is responsible for PVC instability. All curves show the same shape. The mass loss rate increases with temperature and goes through a maximum corresponding to a temperature noted as T_{max} . This latter shifts to higher

temperatures as the plasticizer content increases (see Table I).

Beyond that temperature, the mass loss rate decreases and reaches a zero value around 350°C for all samples. This is due to the reticulation of the remaining sample (polyacetylene obtained) after all plasticizer migration and HCl evolution.

By comparing thermograms of samples having a plasticizer content of 40 phr (DOP, DIDP, and DOP + DIDP), we observe (Fig. 9) that for temperatures below T_{\max} , the mass loss rate is more important for samples plasticized with DOP. This observation is reversed for temperatures higher than T_{\max} .

CONCLUSION

Results exploitation of the present study allowed us to make the following conclusions: 1. Dielectric properties depend on the plasticizer nature as well as on its content. 2. Use of a plasticizer blend induces a synergetic effect on the dielectric properties, such a synergism is illustrated by a lower dielectric loss and a better thermal stability, allowing the sample use in the electric cable.

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