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Studies of Degradation of Plasticized Polyvinyl Chloride (PPVC)

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ABSTRACT
Commercial plasticizers are introduced in Polyvinyl Chloride (PVC) to obtain flexibility, high elongation to break, durability, resistance to heat and chemicals. Very used plasticizers are phthalates, most commonly phthalate being di-2-ethyl hexyl phthalate (DEHP). The phthalates are not chemically bound to PVC and can migrate from different devices and objects due to the influence of temperature, or to other types of degradation. In article are presented the harm effects of phthalates. Through Differential Scanning Calorimetry (DSC) the degradation and emission of additives (phthalates) from PPVC used as insulation (type I) of low voltage cables is studied. It makes a comparative experimental study of DSC curves, mechanical characteristics (tensile strength, elongation at break, modulus of elasticity) and electrical characteristics (volume resistivity, permittivity, losses) of PPVC for insulation, jacket (PPVC type M) and Unplasticized PVC (UPVC). It is considering the possibility of performing numerical analysis on permittivity and losses of PPVC (dielectric mixtures of PVC and phthalates).

Keywords - Differential Scanning Calorimetry, mechanical and electrical characteristics, phthalates and additives, Plasticized, Unplasticized Polyvinyl Chloride

I. INTRODUCTION

PVC is one of the very used polymers after polyethylene (PE) and polypropylene (PP), the most important applications being the building and construction sector [1]. However, the production of PVC creates and releases one of the *most toxic chemicals-dioxin,* which contaminates the environment. Must also be remembered that in PVC additives and plasticizers are introduced. PVC is alone in polymer chemistry being able to both accept and retain large quantities of plasticizer and have its properties modified as a result. Apart from a small region of antiplasticization at very low plasticizer levels, the increase in flexibility is proportional to the level of plasticizer [2].

About 90% of all commercial plasticizers are used in PVC, among the obtained advantages being the flexibility, high elongation to break, durability, resistance to heat and chemicals, resistance to extreme temperatures, color and low melt viscosity compared with PVC with lower levels of plasticization. The characteristics of PPVC are different compared to those of UPVC. This makes the areas of application to be different. Even PPVC is flexible, at the same time is durable and has a low cost. Disadvantages of PPVC are: poor flammability characteristics, very low tensile strength and modulus compared with PVC with lower levels of plasticization.

As a flexible plastic, PVC is used to produce a wide variety of piping. Larger PPVC pipes are often used in plumbing to distribute non-potable water, cable sheathing, including cables in nuclear plants, gaskets, terminal shrouds, food packing applications, footwear, stationery goods, flooring and wall-coverings, carpets, clothing, cosmetics, personal care products, pharmaceuticals, automobiles, herbal preparations, toys. Medical applications are major PPVC application as medical tubing, blood bags, containers with blood, etc. Within the transport sector, which includes automobiles, a lot of studies related to PVC and competing material systems have been undertaken, but most are not publicly available [1].

II. PPVC AS INSULATION AND JACKETING OF CABLES AND WIRES

In the electrical and electronic equipment sector PPVC plays a predominant role in cable applications, **very few studies being available**. PPVC cable seems to have no important competitors in many of its cable applications. A comparison of different applications levels (low, medium voltage) may be of importance. It is unknown whether there are significant differences in environmental performance between the different cable systems within the various applications. The potential environmental effect is large, as the market volume of PVC in this sector is high, but the costs continue to drive the material decision [1].

PPVC is today's most widely used electrical insulation material, not only for protecting wires in thousands of everyday machines and appliances but also as the preferred insulation and sheathing for data transmission cables and fiber optics [3, 4]. In Europe, about 25% of all flexible PVC is used in the production of wire and cables for the electrical industries. The addition of plasticizers provides the required flexibility, improving PVC melt viscosity and increasing production speeds, resulting in better workability. They are very important for energy cables used in buildings and for power distribution wiring buried underground which must remain flexible even at low temperatures. The overall costs of the finished product can be kept relatively low because the complex equipments used by wire and cable producers for extruding PVC does not require high levels of investment. Metals like copper or aluminium account for over 50% of a cable value, that is why all flexible PVC cables are recycled in plants specialised in electrical cable recycling [3].

III. PHTHALATES USED AS PLASTICIZERS

A. Some of the most used plasticizers are phthalates.

Phthalate are esters of phthalic acid (Fig. 1). The most commonly used phthalates and the molecular weight (g/mol) in increasing order are [5]:

DMP (Dimethyl phthalate)	194.18 (g/mol)
DEP (Diethyl phthalate)	222.24
DAP (Diallyl phthalate)	246.26
DPP (Di-n-propyl phthalate)	250.29
DBP (Di-n-butyl phthalate)	278.34
DIBP (Diisobutyl phthalate)	278.34
BCP (Butyl cyclohexyl phthalate)	304.38
DNPP (Di-n-pentyl phthalate)	306.40
BBP (Buthyl-benzyl-phthalate)	312.36
DCP (Dicyclohexyl-phthalate)	330.42
DNHP (Di-n-hexyl-phthalate)	334.45
BDP (Butyl-decyl-phthalate)	362,50
DEHP or DOP(Di 2-ethylhexyl phthalate)	390.56
DNOP (Di(n-octyl) phthalate)	390.56
DIOP (Diisooctyl phthalate)	390.56
ODP (n-Octyl n-decyl phthalate)	418.61
DINP (Diisononyl phthalate)	418.61
DPHP (Di(2-propylheptyl) phthalate)	446.66
DIDP (Diisodecyl phthalate)	446.66
DUP (Diundecyl phthalate)	474.72
DIUP (Diisoundecyl phthalate)	474.72
DTDP (Ditridecyl phthalate)	530.82
DIUP (Diisoundecyl phthalate)	530.82

In reality, the number of phthalates is much higher than those presented. DEHP, also called DOP, is the most widely used, accounting for more that 50% of all phthalates used in PVC globally, do to plasticizing performance and low cost (Fig. 1).

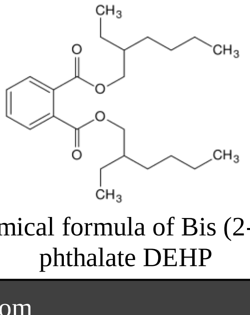


Fig. 1. Chemical formula of Bis (2-ethylhexyl) phthalate DEHP

Uses of the various phthalates depend in part on their molecular weight:

- Higher molecular weight DEHP, DIDP, and DINP are the phthalates produced in highest volume for use in construction, clothing, children's toys, medical devices, cables and wires and household furnishings.
- Relatively low molecular weight phthalates, DBP, DEP, DMP, tend to be used as solvents and in adhesives, waxes, inks, cosmetics, insecticides, and pharmaceuticals [6].

Phthalates (particularly DEHP) lubricate, act as solvents, but are not chemically bound to PVC (Fig. 2). There is no covalent bond between the phthalates and plastics. They are physically bound (weak O..H electrostatic interactions) into the plastic as a result of the heating process.

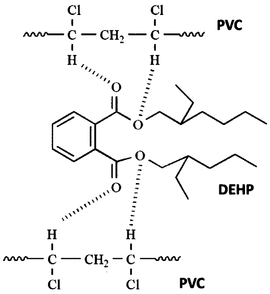


Fig. 2. The weak O..H electrostatic interactions between DEHP and PVC

B. They can migrates from different devices and objects with time or dissolve upon contact with liquids or fats.

Once in the environment, phthalates bind to particles and can be carried in the air over long distances. In general, they do not persist in the outdoor environment due to biodegradation, photo-degradation, and anaerobic degradation; urban indoor air concentrations of phthalates are higher than outdoor air concentrations (for example interior of the cars) [7]. DEP and DMP are present in higher concentrations in air in comparison with the heavier and less volatile DEHP. PVC flooring produce high concentrations of BBP and DEHP.

IV. HARM EFFECTS OF PHTHALATES

Has been shown since 1980 that many phthalates cause harm effects and are considered to be among the most universal of all environmental pollutants. Human exposure to phthalates can occurs through inhalation, ingestion, intravenous injection, medication [7] and skin absorption from contaminated air, water, soil and food [8, 9]. From PPVC phthalates bags could leach into food and cause harm effects, could cause harm effects on the environment, an increased incidence of liver tumor (experiences in rats and mice), can influence human reproductive system and function of hormones in the human body [10,11]. Exists researches who showed that bronchial obstruction in children was directly related to the amount of plasticizer-emitting material present in the house, strong links between allergies and DEHP and BBP in all children's articles. Is reviewed the evidence for the role of exposure to phthalates from PVC flooring products in the development of asthma and allergies [12, 13,14].

Is why in 2005, the EU permanently banned the use of DEHP, DBP and BBP in all children's articles [15]. In 2007 the EU banned the use of DINP, DBP and DNOP in children's articles which can be put in the mouth. In 2011 six substances including DEHP, BBP and DBP have been listed for Authorization in Annex XIV of Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) by Regulation (EU) No 143/2011. According to the regulation, phthalates including DEHP, BBP and DBP will be banned from February 2015 [16].

Nuclear irradiation of blood bags, commonly used for sterilizing PVC, produced DEHP degradation and migration from PVC sheets. Studies has indicated that sterilization DEHP in blood bags is hydrolyzed by esterase into mono (2-ethylhexyl) phthalate MEHP, which is thought to be more toxic than the parent compound [17]. DEHP can removed too by exposure to severe heat or using strong solvents.

V. PPVC AND UPVC SAMPLES

In Fig. 3. a,b are represented two low voltage cables with PPVC insulation and jackets. From insulation and jackets of the cables have been cut samples with a mass of order mg. Samples were also cut from plates of UPVC. Their weight was determined with analytical balance [19].

a. b

Fig. 3. a,b. Low voltage cables with PPVC insulations and jackets

1-conductors; 2-insulation; 3-jacket

VI. DSC MEASUREMENTS

Differential scanning calorimetry or **DSC** is a technique to study what happens to polymers when they're heated. DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment (Fig. 4).

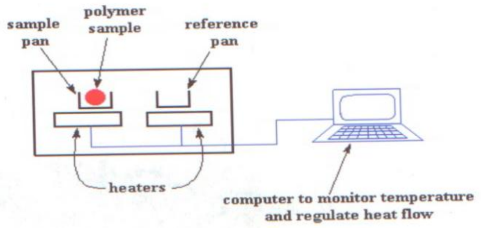


Fig. 4. Schema of DSC measurements

VII. MEASUREMENTS OF MECHANICAL AND ELECTRICAL CHARACTERISTICS

There is a significant dependence between mechanical characteristics and the content of phthalates in PVC. The static tensile strength σ, the relative elongation at break, the modulus of elasticity E were determined. Samples are represented in Fig. 5, according to SR EN ISO. If l_0 is the initial length of the sample and Δl is the absolute elongation at break, the relative elongation at break is: $\varepsilon = \Delta l / l_0$. Hooke law expresses the relation between these quantities: $\sigma = E \cdot \varepsilon$. To determine the mechanical characteristics testing machine was used.

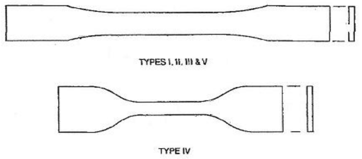


Fig. 5. Samples for mechanical measurements from PPVC insulation of low voltage cables according to SR EN ISO

C. Electrical measurements.

For using PPVC as insulation in the construction of cables and wires is important to be determined volume resistivity ρ_V, permittivity ε (dielectric constant or relative permittivity, 50Hz), loss tangent tg δ (50Hz). Were used characteristic electrodes (Fig. 6).

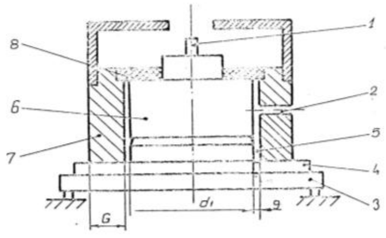


Fig. 6. Electrodes used to determinate the electrical resistances:

1-terminal to the apparatus of measurements; 2-terminal for earth connection; 3-terminal for voltage application; 4-sample; 5-security space; 6-protected electrode; 7-guard electrode; 8-press for guiding and isolation

R_V volume resistance measured between two electrodes applied on the opposite faces of a sample is the ratio of the voltage applied to the electrodes and the current through the sample. Resistance measurement was made with an ultra-megometru using a 500V DC source. Installation allowed measurement of high resistances: ($10^9 \div 10^{13}\,\Omega$) order.

The volume resitivity ρ_V in the case of the electrodes of Fig. 6 is:

$$\rho_V = \frac{R_V S}{l}, \quad S = \frac{\pi d_2^2}{4} = \frac{\pi (d_1 + g)^2}{4}$$

where R_V is volume resistance, *S* is the nominal area of the used electrodes, *l* is the average thickness of the sample. The precision of determining the resistance was $\pm 5\%$. Electrical characteristics for frequency *f* = 50Hz presents a major interest, both in terms of theoretic and practical aspects, since as insulating materials are used in high voltage at this frequency. Classical equipment used in this case for measuring permittivity and losses was Schering bridge voltage max. 6KVAC with fixed frequency of 50Hz. The equilibrium of the bridge is achieved by means of variable resistance and a variable capacitor C_4 in parallel with the resistance R_4. Relative permittivity is:

$$\varepsilon = C_x / C_0,\ \mathrm{tg}\,\delta = \omega R_4 C_4,\ \omega = 2\pi \cdot f,\ f = 50\mathrm{Hz},$$

C_x is the capacity with dielectric, C_0 is the capacity whith air. The precision of determining the capacity was ±1%, the precision of determining tgδ was $\pm 1 \cdot 10^{-5}$.

VIII. EXPERIMENTAL RESULTS AND DISCUSSION

In Figures 7÷10 are represented DSC curves for PPVC insulation and jackets of low voltage cables. In Figure 7 complex peak is observed who indicates the glass transition domain for PPVC: the onset is 53.3ºC and the end 91.9ºC, the glass transition temperature being near T_G = 81.2ºC. In Figure 8 it is observed that, after the heating at 170ºC of PPVC insulation, the glass transition temperature increased to the value T_G = 115.0ºC. This is due to the degradation of PVC and emission of plasticizers (phthalates) and additives. In this case the onset of the glass transition domain is 83.1ºC and the end 146.8ºC.

By cooling the sample at 20ºC and the second heating to 170ºC is obtained the graph in Figure 9. In this case we obtain a very large domain of transition with T_G near 144.3Cº, thus a new increase of glass transition temperature and a new emission of phthalates and additives. The plasticizers increase the distance between polymer chains, increase their mobility and flexibility thus significantly decrease of T_G. The emission of phthalates can be considered as a phenomenon of evaporation and described with relationship Hildebrand [18]. The solubility parameter δ is the square root of the cohesive energy density:

$$\delta = \sqrt{\frac{\Delta Hv - RT}{V_m}}.$$

The cohesive energy density is the amount of energy needed to completely remove unit volume of molecules to infinite (ideal gas). This is equal to the heat of vaporization divided by its molar volume V_m in the condensed phase.

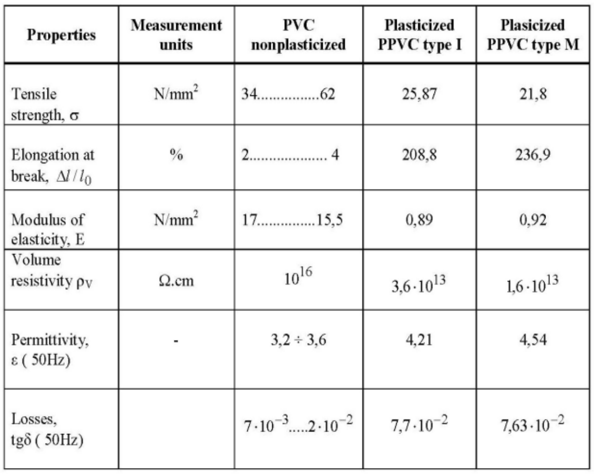
The low value T_G of PPVC jacket from Figure 10 is due to a large percentage of phthalates, to obtain a high flexibility.

In Fig. 11 is presented the glass transition domain of UPVC samples: between 81.9ºC and 92.0ºC, glass transition temperature being T_G =86.5ºC. The high value can be explained by the small amount of plasticizers [19].

Using the results from the literature, Babrauskas [20] shows that the loss of plasticizer by thermal degradation occurs at moderate temperature. Anandakumaran and Stonkus [21] studied plasticizers loss in commercial PPVC and found that about 25% was lost by heating at 120ºC. Zaikov [22] remarks that the loss of plasticizer causes formation of voids in the material which reduce the breakdown strength of the insulation.

In table 1 is observed that the elasticity modulus *E* values deacreases with increasing plasticizer content, that occurs due to increased flexibility, according to the Hooke law. The important elongation at break increases are due to increased flexibility. Tensile strength σ is slightly higher for non-plasticized PVC.

Table 1. Mechanical and Electrical Properties Of Upvc And Ppvc Type I And Type M



Properties	**Measurement units**	**PVC nonplasticized**	**Plasticized PPVC type I**	**Plasicized PPVC type M**
Tensile strength, σ	N/mm^2	34...............62	25,87	21,8
Elongation at break, $\Delta l / l_0$	%	2................... 4	208,8	236,9
Modulus of elasticity, E	N/mm^2	17..............15,5	0,89	0,92
Volume resistivity ρ_V	Ω.cm	10^{16}	$3{,}6 \cdot 10^{13}$	$1{,}6 \cdot 10^{13}$
Permittivity, ε (50Hz)	-	3,2 ÷ 3,6	4,21	4,54
Losses, tgδ (50Hz)		$7 \cdot 10^{-3}$.....$2 \cdot 10^{-2}$	$7{,}7 \cdot 10^{-2}$	$7{,}63 \cdot 10^{-2}$

Due to introduced plasticizers resistivity ρ_V decreases, while permittivity ε and losses tg δ increase. Be observed close values of electrical measurements for type I and type M PPVC.

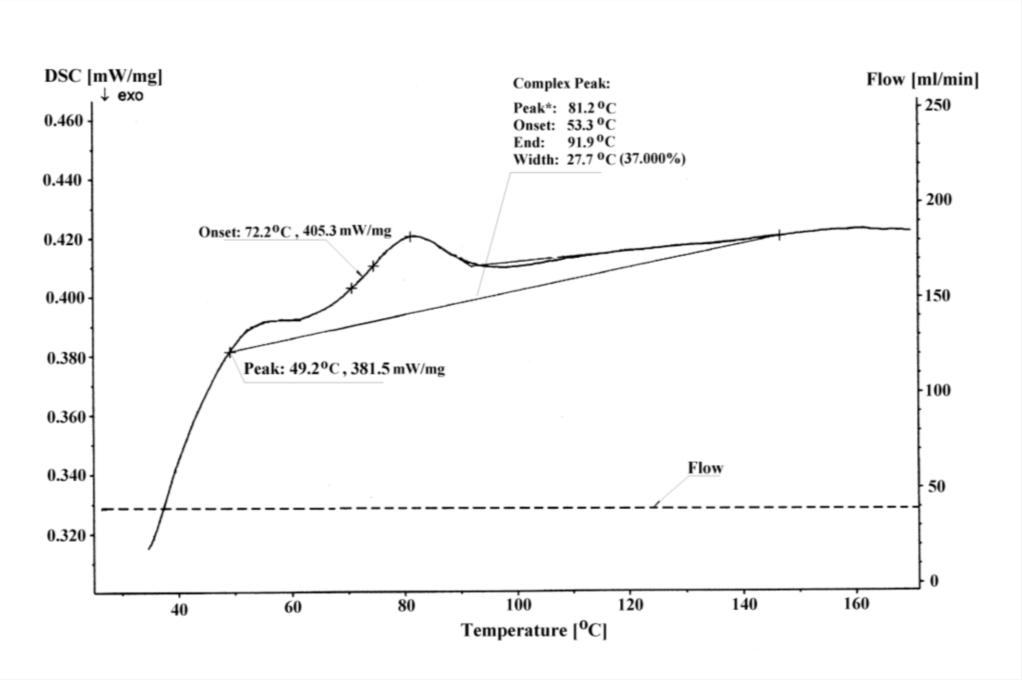


Fig. 7. DSC dependence on temperature of PPVC of low voltage cable

The glass transition temperature is near 81.2ºC

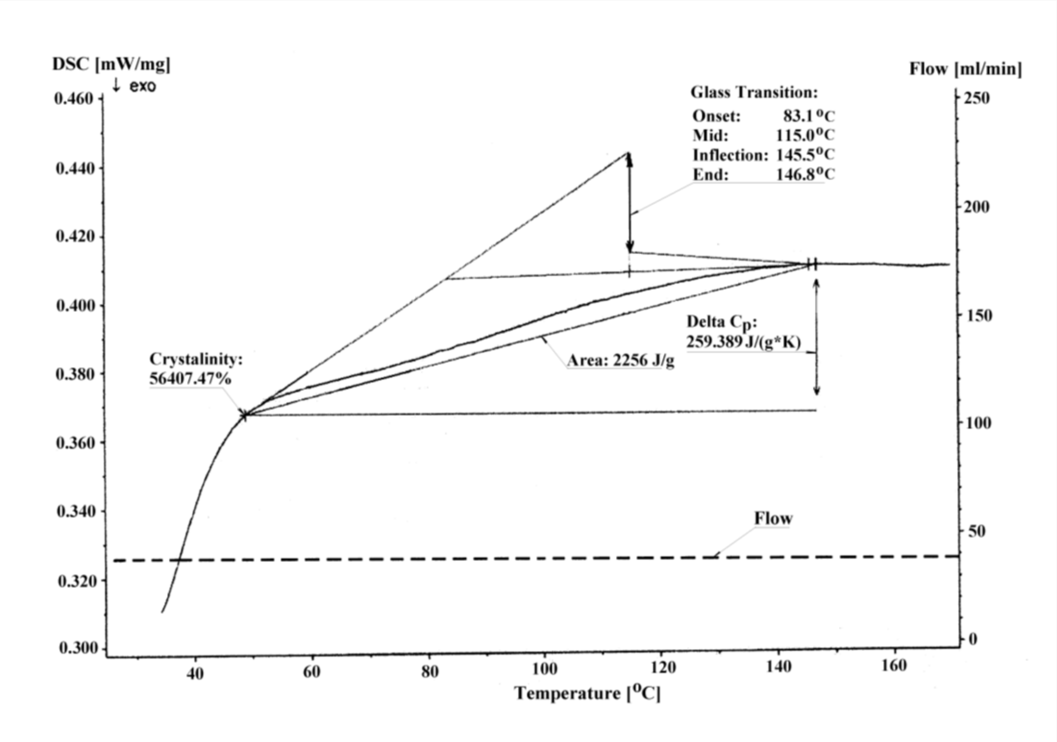


Fig. 8. DSC representation for PPVC cable insulation of low voltage cable after degradation by thermal heating up to 170ºC

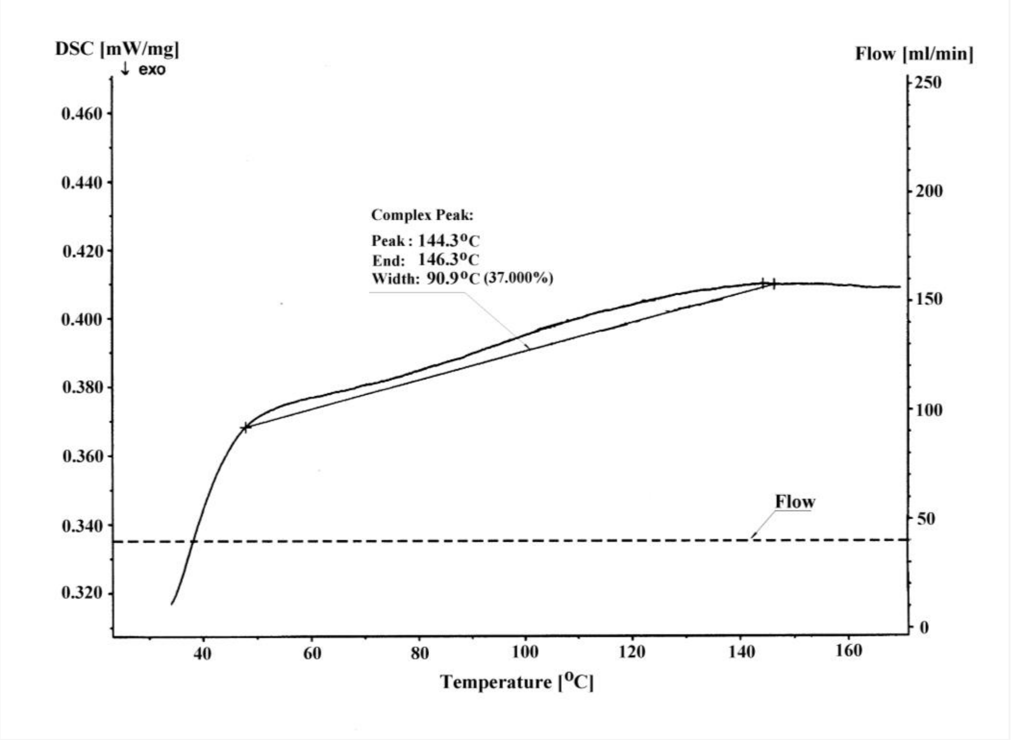


Fig. 9. DSC for PPVC cable insulation of low voltage cable after degradation by thermal heating up to 170ºC, cooling to 20ºC and a new thermal heating up to 170ºC

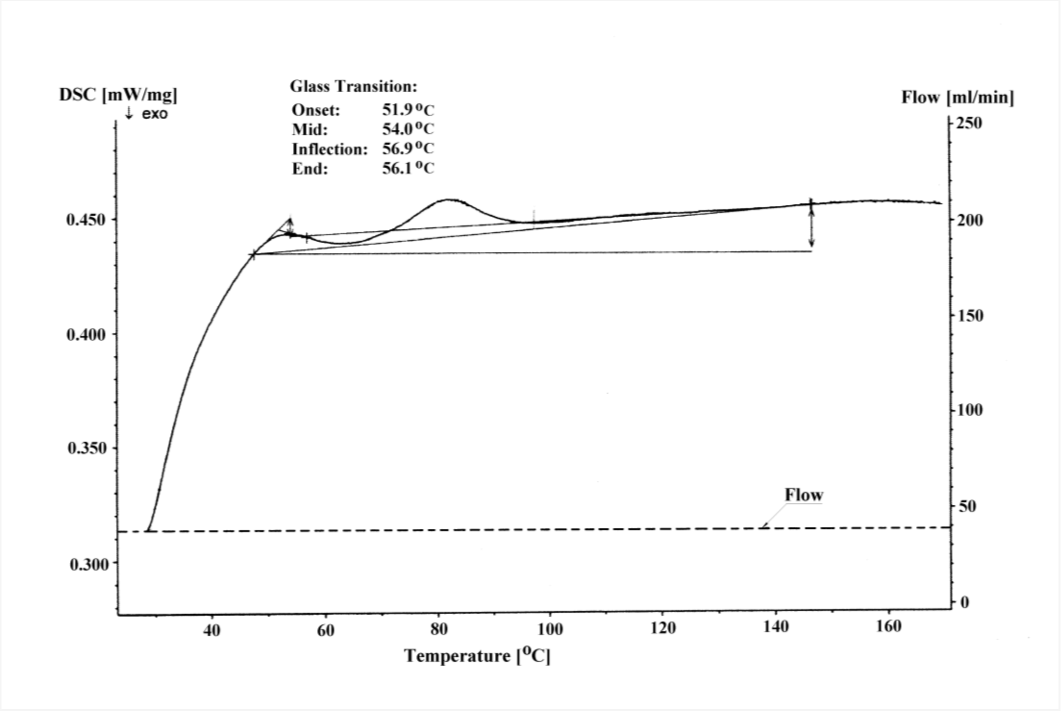


Fig. 10. DSC dependence for PPVC cable jacket of low voltage cables. Glass transition temperature is 54.0ºC

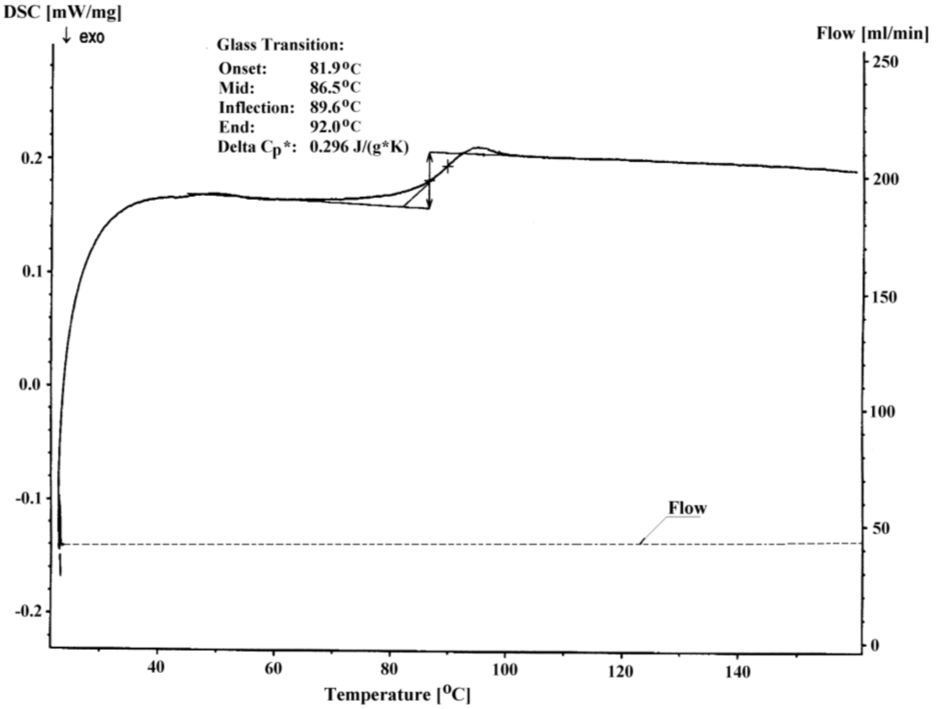


Fig. 11. DSC dependence of temperature of UPVC

IX. NUMERICAL ANALYSIS IN DIELECTRIC MIXTURE PVC AND PHTHALATES.

The main problems studied in dielectric mixtures are:

- The determination of the permittivity of the homogeneous mixture by knowing the permittivity of the components and their concentration;
- The study of the dielectric response in the frequency domain allowing critical assessment of frequency peaks where losses occur (especially at very low frequency) and the order of magnitude of these losses.

Using Ampere equation: $\nabla(\underline{\varepsilon} - j\sigma/\omega\varepsilon_0)\vec{E}=0$, with a time-varying electric field $E = E_0\exp[j\omega t]$, we obtain the average complex permittivity of the mixture:

$$\underline{\varepsilon}_m = \varepsilon' - j\varepsilon'',$$

$$\underline{\varepsilon}_m = \tilde{D}/\tilde{E}$$

From the formula of electrostatic energy:

$$\frac{1}{2}\underline{\varepsilon}_m\tilde{E}^2 = \frac{1}{\Omega}\int_{\Omega}\frac{1}{2}\tilde{E}\cdot\tilde{D}\,\mathrm{d}\Omega$$

where Ω is the computational domain, we can obtain too the average complex permittivity of the mixture:

$$\tilde{E} = \frac{1}{\Omega}\int_{\Omega}E\cdot d\Omega,\quad \tilde{D} = \frac{1}{\Omega}\int_{\Omega}D\cdot\mathrm{d}\Omega.$$

X. CONCLUSIONS

DSC studies allow the study of PVC degradation pointing the existence and emission of phthalates and additives from PPVC insulation and of low voltage cables. More detailed studies are needed, especially chromatographic studies, for identification and quantitative determinations. Quantitative studies are needed to perform numerical analysis mentioned.

The emission of phthalates leads to the increase of glass transition domain and to the increase of glass transition temperature.

Is observed that the elasticity modulus values deacreases with increasing plasticizer content, that occurs due to increased flexibility. Important elongation at break increases due to increased flexibility. Tensile strength σ is slightly higher for non-plasticized PVC.

Due to introduced plasticizers resistivity decreases, while permittivity and losses increase. Was observed close values of electrical measurements for type I and type M PPVC

Since the leaching of phthalates from PPVC products is an uncontrollable source of contamination, is necessary to eliminate phthalates at source. Can be used alternative polymers which does not contain commercial phthalates or any other softeners.

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