

STUDIES ON THERMAL AND RADIATIVE DEGRADATION OF UNPLASTICIZED POLYVINYL CHLORIDE

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Abstract. *The paper studies the degradation of Unplasticized Polyvinyl Chloride (UPVC) due to the influence of the temperature and nuclear γ radiations in the domain 0-50 Mrad. Differential Scanning Calorimetry (DSC) studies were performed to determine the degradation of PVC for temperatures ranging between 0 and 160°C. We determined the glass transition domain in order to emphasize the changes due to temperature and nuclear γ radiations. Measurements of electrical characteristics and mechanical characteristics for UPVC and Plasticized Polyvinyl Chloride (PPVC) have allowed a comparative study. Thermal degradation was manifested by the increase of the glass transition temperature due to the emission of additives (particularly phthalates). In the case of the dose of 5.44 Mrad of nuclear gamma radiations, important changes occur in UPVC. The degradation caused by irradiation with doses of 16.0 and 50.0 Mrad have been emphasized.*

Keywords: Unplasticized and Plasticized PVC, additives, degradation, temperature, γ radiations.

1. Introduction

Polyvinyl Chloride (PVC) is one of the most used polymers with polyethylene (PE) and polypropylene (PP), the most important applications being the building and construction sector.

In 1998 in Europe ca. 5.5 million tons of PVC polymer were used: one third of the total production for the production of flexible, plasticized PPVC products and the other two thirds for the category of rigid unplasticised UPVC products [1]. PVC is a controversial plastic material due to its hazardous impacts on the environment and human health. Very large quantities of hazardous organochlorine by-products are formed and released into the environment, formation that begins with the production of chlorine gas generated during the synthesis of ethylene dichloride (EDC) and vinyl chloride monomer (VCM), the feedstocks for PVC. Further by-products are created and released into the environment during the incineration of hazardous wastes from EDC and VCM production, the incineration of vinyl products in the waste stream, the recycling of vinyl-containing metal products by

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combustion and the accidental burning of PVC in fires in buildings, warehouses, or landfills. Among the most important by-products of the PVC lifecycle are dioxin and a large group of structurally and toxicologically related compounds, collectively called "*dioxin*" or "*dioxin-like compounds*" [2, 3]

By-products of PVC production and during their life cycle are highly persistent, bioaccumulative, and toxic, having negative effects on the environment, human health and other living organisms. Some effects on human organisms: they cause cancer and the disruption of the endocrine system, affect human reproduction, cause bronchial obstruction in children and allergies.

In order to reduce the thermal and photochemical instability of virgin PVC, a number of additives are applied before manufacturing PVC products: heat stabilizers, plasticizers, inert fillers, pigments, impact modifiers, lubricants, UV stabilizers, biocides (to prevent fungal growth on flexible PVC), and antistatic agents [4, 5]. The percentage of additives varies between 10 and 25% in weight, in the case of UPVC. Flexible PPVC can contain plasticizers up to 60% of the weight, the average content being about 30%. Stabilizers (1÷8%) prevent thermal UV degradation and hydrogen chloride evolution during processing and confer heat and UV stability [6, 7]. The most important stabilizers are: lead compounds (60÷75% of stabilizers for PVC in Europe); organotin stabilizer (10÷15%) barium/zinc, calcium/zinc [8]. The plasticizers are added to the resin in variable quantities in order to obtain a flexible and soft PVC, among the obtained advantages being the high elongation to break, durability, resistance to heat.

A category of plasticizers worldwide used are the phthalates which are esters of phthalic acid [9]. DEHP (Di 2-ethylhexyl phthalate), also called DOP, is the most widely used, accounting for more than 50% of all phthalates used in PVC globally, due to its plasticizing performance and to its low cost. The phthalates are not chemically bound to PVC and can migrate in time from different devices and objects under the influence of temperature, due to other types of degradation, 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.

It has been shown since 1980 that many phthalates cause harm effects [10, 11]. Phthalates are considered to be among the most universal of all environmental pollutants. Human exposure to phthalates can occur through inhalation, ingestion, intravenous injection, medication and skin absorption from contaminated air, water, soil, food, cosmetics [12, 13]. It is why in 2005 and 2007 the EU permanently banned the use of DEHP and other phthalates in all children's articles. According to the Regulation (EU) No 143/2011 phthalates including DEHP, were banned since February 2015 [14-16].

Very important domains of the use of UPVC are: replacement for wood in construction, windows and doors frame and sills, the majority of plastic pipes in the world, medical and dental pieces etc.

Use of PPVC: to distribute non-potable water, cables and wires, food packing, footwear, stationery goods, flooring and wall-coverings, carpets, clothing, cosmetics, personal care products, pharmaceuticals, automobiles, herbal preparations, toys, etc.

The temperatures of resistance to heat are in the range of: 65-80°C (UPVC) and 60-103°C (PPVC). PVC starts to decompose at 140°C, melting temperature starting from about 160°C. PVC is a classical amorphous polymer.

A new sustainability initiative “Vinyl Plus” was developed with the following goals: a quantum leap in recycling rates of PVC and in achieving the development of innovative recycling technologies, addressing concerns about organochlorine emissions, ensuring the use of additives based on sustainability criteria, increasing energy efficiency and the use of renewable energies and raw materials in PVC production. PVC is capable of playing an important role in sustainable development, because of considerable improvements in raw material and energy efficiency and in the current ecological profiles on manufacturing PVC [17].

2. Glass Transition Temperature

The glass transition is a property of amorphous solids or of the amorphous portions of a semi - crystalline solids. According to the temperature, the amorphous regions can be either in the relatively brittle glassy state (solid) or into a molten or rubbery state (liquid). The temperature at which the transition in the amorphous regions between the glassy and rubbery state occurs is called the **glass transition temperature T_G** . The inverse transition occurs through sudden cooling of a viscous liquid and is called **vitrification** [18].

The glass transition temperature of a material is characterized by a domain of wide range of temperatures in which it is produced. T_G is the middle of the domain and is always less than the melting temperature T_m of the crystalline state of the material, if it exists. T_G is the most important property of a polymer and is directly related to its mechanical properties (strength, hardness, toughness, brittleness, elongation, modulus of elasticity). The most prominent change in the macroscopic behavior of amorphous polymers is the glass-rubber relaxation where the rigid glassy solid material becomes a viscoelastic fluid.

2.1. Factors Affecting the Glass Transition Temperature

T_G is a parameter difficult to be defined and *its exact measurement is not easy* [19, 20]. No theory (including that based on free volume, on thermodynamics, the kinetics, or complex statistics) can not completely explain the macroscopic phenomenon that occurs near T_G [21-24].

T_G depends on many factors:

- the polymer structure;
- the mobility of the polymer chain, more immobile is the chain, higher is the value of T_G . Anything that restricts rotational motion within the chain should raise T_G ;
- the flexible groups increase the flexibility of the chains and reduce T_G ;
- flexible pendant groups tend to limit the proximity of the chains and lowers T_G ;
- chain stiffness and stiffening groups in the polymer chain reduce the flexibility of the chain and raise the value of T_G ;
- bulky pendant groups (benzene ring) restrict rotational freedom and increase T_G ;
- stronger intermolecular forces lead to a higher T_G (the C-Cl bond from PVC);
- the crosslinks between chains restrict rotational motion and raise T_G ;
- plasticizers (low molecular weight compounds added to plastics to increase their flexibility) lower T_G ;
- the molecular weight and the molecular weight distribution of the polymer;
- the thermal history of the material, the rate of heating / cooling and deformation: more heating rates / cooling or solicitations lead to higher values of T_G ;
- the pressure.

2.2. Thermodynamics of Thermal Transitions

The glass transition can be considered an Ehrenfest second-order transition as a discontinuity in the second derivatives of the Gibbs free energy G :

$$\begin{aligned} \left(\frac{\partial^2 G}{\partial T^2} \right)_p &= \left(\frac{\partial S}{\partial T} \right)_p \\ \left(\frac{\partial^2 G}{\partial p^2} \right)_T &= \left(\frac{\partial V}{\partial p} \right)_T \end{aligned} \quad (1)$$

where: T is the temperature, p pressure, V the volume, S the entropy.

From the relations (1) it results that if the glass transition is an ideal second-order transition, the volume and the entropy (heat capacity) will change abruptly when the temperature reaches the glass transition temperature. However, for real polymeric systems, the change of these properties, discontinuity or slope, is more gradual and is also affected by the heating rate, i.e. the glass transition is not a true thermodynamic transition but rather a pseudo-second-order transition.

The importance of the heat capacity C_p results from the classical thermodynamic relations [25], U is the energy, C_v heat capacity at constant volume, Q quantity of heat, H the enthalpy, G - Gibbs energy, F free energy, ν the number of the moles.

$$U = \int_0^T C_v dT, \quad C_p = \frac{dQ}{dT} = \left(\frac{dH}{dT} \right)_{p,\nu} \quad (1)$$

$$H - H_0 = \int_0^T C_p dT$$

$$S = \int_0^T C_p dT \quad (3)$$

$$G = H - TS \quad (4)$$

$$F = U - TS. \quad (5)$$

These equations show that the heat capacity is connected to all the thermodynamic properties of the system, which give information about the microscopic motions into the system. The enthalpy H or the energy U gives information about the total thermal motion and the entropy S gives information about the order degree of the system. Finally, the Gibbs or free energy G and F give informations about the stability of the system. All the calorimetric techniques lead to the heat capacity at constant pressure, C_p , while in terms of microscopic quantities, heat capacity at constant volume, C_v , is more accessible quantity.

The relationship between (C_p) and (C_v) is:

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V} \right)_{T,\nu} + p \right] \left(\frac{\partial V}{\partial T} \right)_{p,\nu} \quad (6)$$

3. Experimental details. Samples and method of measurements

We cut samples with different masses and shapes from commercial UPVC and commercial PPVC of low voltage cables, depending on the types of measurements. Their weight was determined with an analytical balance. For DSC measurements the mass of the samples was around 10 mg. For the measurements of mechanical

characteristics the shape of samples was in agreement with SR EN ISO [26]. A testing machine was used.

γ irradiation was performed in air using a source with a fixed irradiation chamber, volume 0.1l. The installation has a source of Cs¹³⁷ and the energy of 0.662 MeV. The dose rate was 8×10^4 rad/h and the domain of radiations 0- 50 Mrad.

The static tensile strength σ , the relative elongation at break and the modulus of elasticity E were determined. If l_0 is the initial length of the sample and Δl is the absolute elongation at break, the relative elongation at break ε is:

$$\varepsilon = \Delta l / l_0 \quad (7)$$

Hook's law expresses the relation between these quantities:

$$\sigma = E \cdot \varepsilon \quad (8)$$

In order to use PVC as insulation in the production of cables and wires it is important to determine the volume resistivity ρ_V , the permittivity ε (dielectric constant or relative permittivity, 50 Hz), loss tangent $\text{tg } \delta$ (50 Hz). Characteristic electrodes were used.

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. The resistance measurements were made with an ultramegohmmeter using a 500 V, DC source. The installation allows to measure high resistances ($10^9 \div 10^{13}$) Ω .

The equipment used for measuring permittivity and losses was a classical Schering bridge, voltage max. 6 kVAC with fixed frequency of 50 Hz. The equilibrium of the bridge is achieved by means of a variable resistance and a variable capacitor C_4 in parallel with the resistance R_4 . The relative permittivity ε and the loss tangent $\text{tg } \delta$ are:

$$\varepsilon = \frac{C_x}{C_0}, \text{tg } \delta = \omega R_4 C_4, \omega = 2\pi f, f = 50\text{Hz} \quad (9)$$

C_x is the capacity with dielectric, C_0 is the capacity with air, f is the frequency, and ω is the angular frequency.

DSC measurements were performed on the calorimeter 200F3, Maia, Netzsch-Geratebau GmbH with a measuring cell; Gas flow control device (N₂); Sealing press; Al samples pans with lids.

4. Discussions

Table 1 compares mechanical and electrical characteristics of UPVC and PPVC (for insulation and jackets of low tension electrical cables). Mechanical characteristics determined were: tensile strength, elongation at break, modulus of elasticity, and electrical characteristics: volume resistivity, permittivity (50 Hz), and loss tangent (50 Hz).

There is a significant dependence between the mechanical characteristics and the content of additives and phthalates in PVC.

Table 1. Comparative experimental data between mechanical and electrical characteristics for UPVC and PPVC (insulation and jackets of low voltage cables)

<i>Properties</i>	<i>UPVC</i>	<i>PPVC Insulation and jackets</i>
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 elasticity E (N/mm ²)	17 ... 15.5	0.89 ÷ 0.92
Volume resistivity ρ_v (Ω cm)	10^{16}	$3.6 \cdot 10^{13} \div 1.61 \cdot 10^{13}$
Permittivity ε (50 Hz)	3.2 ÷ 3.6	4.21 ÷ 4.54
Losses tg δ (50 Hz)	$7 \cdot 10^{-3} \div 2 \cdot 10^{-2}$	$7.7 \cdot 10^{-2} \div 7.6 \cdot 10^{-2}$

The limits from the Table 1 result from the literature [27] and our measurements are in good agreement with them. From the values obtained is observed that PPVC presents high values of elongation at break and low levels of modulus of elasticity. Higher levels of flexibility are due to the high content of phthalates. The addition of additives (phthalates) produces an increase in losses and permittivity.

5. DSC analysis of degradation

From experimental measurements performed on samples of insulation from commercial PPVC used in low voltage cables, we observe the domain of the glass transition temperature: onset 53.3°C, the end 91.9°C, the glass transition temperature is about 81.2°C. After a heating cycle 160°C - cooling at 20°C, and a second heating to 160°C, T_G increased to 115.0°C. This is due to the thermal degradation of PVC and the emission of additives including plasticizers (phthalates). The onset of the glass transition is 83.1°C and the end 146.8°C.

By cooling the sample at 20°C and a new heating to 170°C it was obtained a glass transition temperature of about 144.3°C: a new increase of glass transition temperature and a new emission of additives and plasticizers (phthalates).

For UPVC the glass transition domain is between 71.1°C and 81.6°C, the glass transition temperature being $T_G = 80.6^\circ\text{C}$. (fig. 1). The main maximum: 89.5°C, 0.2249 mW/mg is attributed to the relaxation phenomena that occur due to the glass transition of the material.

In figure 2 are observed four maxima (57.9°C, 64.7°C, 72.1°C and 77.5°C) prior to the main maximum from 89.5°C position. We attribute the four maxima to the different additives introduced in UPVC.

After a heating cycle 160°C - cooling at 0°C, and a second heating at 160°C, we observed changes in DSC curve (fig. 3). It is observed the disappearance of irregularities and of peaks which are prior to the main peak. Glass transition is $T_G = 89.5^\circ\text{C}$ (onset 85°C and end 92.9°C). The growth of T_G can be attributed to the thermal degradation and emission of additives from UPVC due to the increase of the temperature. The maximum of 94.9°C position, energy 0.2118 mW/mg, is also attributed to the relaxation phenomena due to glass transition.

It could be considered that the primary process of thermal degradation of UPVC includes: (1) initiation of dehydrochlorination; (2) the elimination of HCl and the simultaneous formation of conjugated double bond; (3) the termination of dehydrochlorination [28].

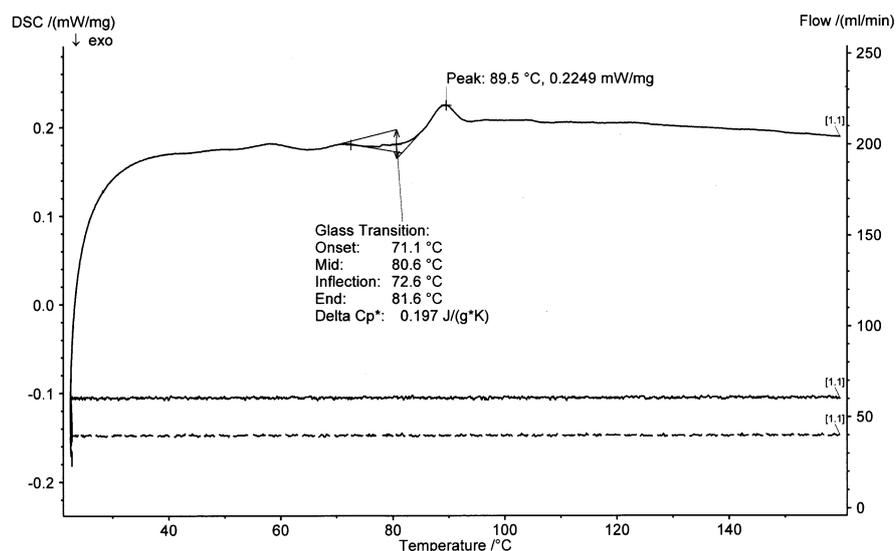


Fig. 1. DSC dependence on temperature for UPVC.

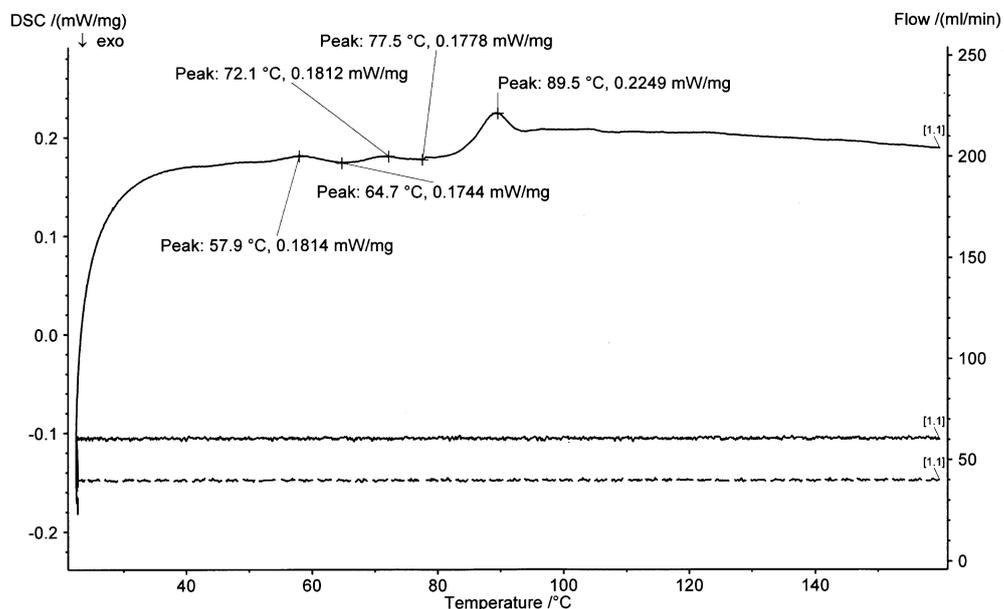


Fig. 2. DSC dependence on temperature for UPVC and the main maximum from 89.5°C position. Is observed the existence of four maximum before it.

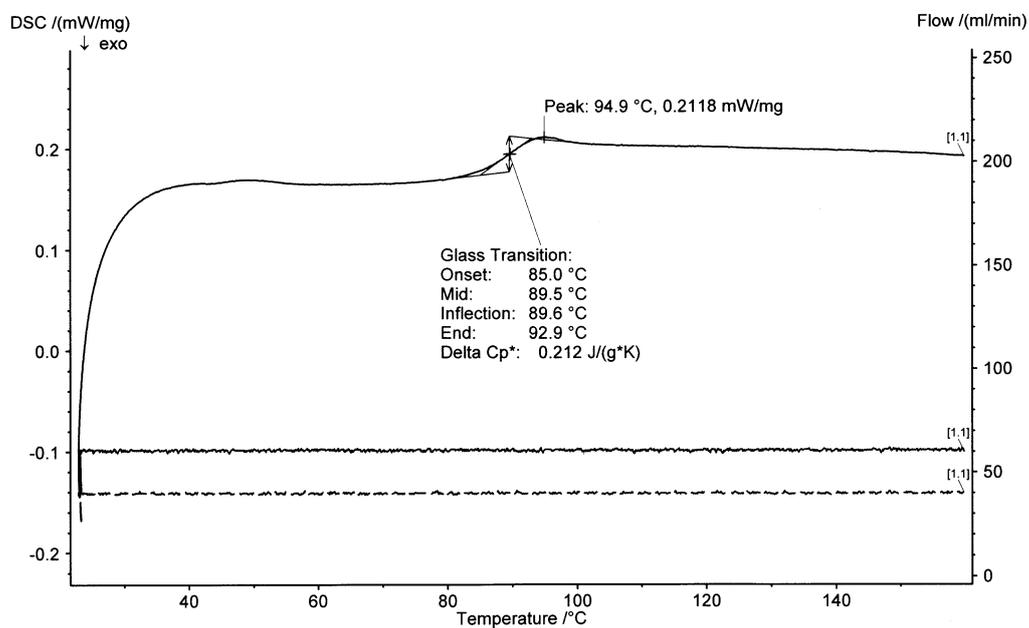


Fig. 3. DSC dependence on temperature for UPVC after cooling /second heating at 160°C.

The evolution of HCl takes place by its elimination from the polymer backbone, while the discoloration is due to the formation of conjugated polyene sequences of 5 to 25 double bonds. The process starts at the glass transition temperature by elimination of HCl, which is the main volatile product up to about 330°C. The processing of PVC at elevated temperatures requires the use of thermal stabilizers which incorporate toxic heavy metals (lead) organotin stabilizers and combinations of calcium, barium salts with zinc systems. Some of these stabilizers have disadvantages related to toxicity, environmental pollution and high cost.

6. Influence of the γ nuclear radiations

The current opinion is that not only the crosslinking of polymers is important for industrial applications but also their degradation. Special attention was given to the Control of Degradation Effects in Radiation Processing of Polymers, important discussions taking place about: molecular weight modification, bulk properties modification, and surface modification (IAEA: International Atomic Energy Agency) [29]. It is why we performed measurements on γ irradiated in air UPVC samples with radiation dose of 5.44, 16.0 and 50.0 Mrad.

From long time ago it is known that polymeric substances are considerably more sensitive to radiations compared to the metals and ceramics. Significant effects are to be expect. Polymeric substances exhibit a wide variety of radiation effects. The formation of new chemical bonds after irradiation usually results in irreversible effects. These are manifested as changes in appearance, chemical and physical states and mechanical, electrical, and thermal properties. However, not all properties of a polymer are affected to the same degree by radiation. The radiation stability of a polymer is dependent upon the chemical structure of the material [30].

Irradiation creates free radicals which can recombine forming crosslinks. At the same time a competing process called scissioning occurs, the polymer chains are broken and molecular mass decreases. One of these processes may predominate over the other, depending upon the polymer and the dose. The rate of occurrence for these two processes is the efficiency value G , defined as the number of events that occurs with the absorption of 100 eV.

The crosslinking process results in the formation of chemical bonds between two adjacent polymer molecules. This reaction increases the molecular weight of the polymer until the material is eventually bound into an insoluble three-dimensional network. The degree of crosslinking depends upon the radiation dose; one of the benefits is that the degree of crosslinking can be easily controlled by the amount of dose [31]

Chain scission, or fracture of polymer molecules, decreases the molecular weight and increases solubility [32, 33]. In general, chain scission results in a decrease in Young's modulus, reduced yield stress for plastic flow, increased elongation, decreased hardness, and decreased elasticity. It sometimes causes embrittlement and release of gas.

It must to take into account the effect of nuclear radiation on the additives, oxidation phenomena occurring during irradiation in air but also after the termination of irradiation. Oxidation phenomena are more intensive in the case of γ irradiation than in the case of other types of radiations. [34-36].

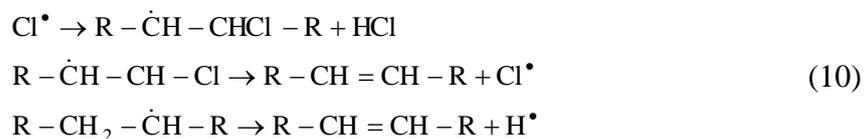
PVC is a polymer radiation crosslinkable, $G = 0.3$, in air irradiation [37].

In the case of PVC were recently studied: off-gasing of corrosive HCl and H₂; yields and post irradiation behaviour; structural degradation; change in molecular weight and distribution of polymer chain lengths; formation of conjugated C=C systems; oxidation and production of C=O cromophores [38].

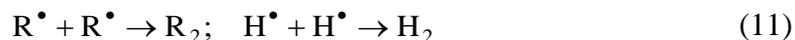
As results of irradiation the reactions that occur are:

Initiation reaction: C-Cl scission;

Radical reactions (propagation):



Terminal reactions: HCl evolution (free radical mechanism) and formation of H₂ from atom precursors:



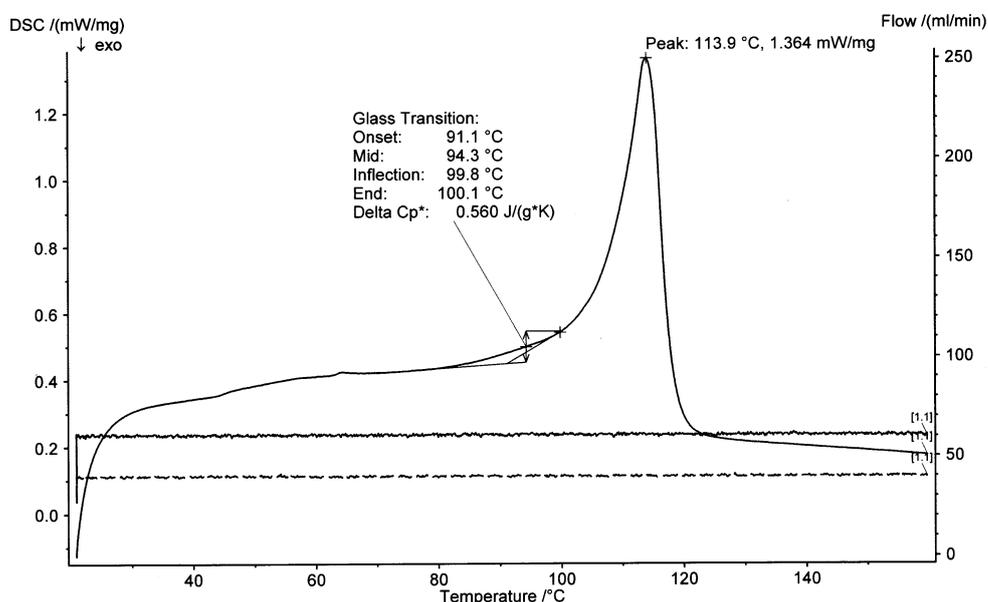


Fig. 4. DSC dependence on temperature for UPVC samples irradiated with γ radiations at 5.44 Mrad.

Figure 4 represents the observed DSC dependence on temperature for UPVC samples irradiated with γ radiations at 5.44 Mrad for temperatures (0-160)°C. Important changes are observed. There is an important increase of glass transition temperature T_G for 5.44 Mrad (94.3°C) compared to the same temperature for 0 Mrad (80.6°C).

Also is established the important growth of the values onset and end of the domain of glass transition: 91.1°C and 100.1°C. It is observed a significant peak at 113.9°C, with high energy 1.364 mW/mg, indicating a significant increase in relaxation phenomena.

We consider that for this dose of radiation (5,44 Mrad) important crosslinking events occur. The presence of crosslinks between chains restricts rotational motion and raises T_G .

By increasing the radiation dose at 16 and 50 Mrad we obtain a decrease of glass transition temperature: 77.8°C, respectively 77.5°C (figs. 5 and 6). Main peaks relaxation positions 90.1°C and 89.2°C of weak intensity 0.2575 mW/mg, 0.2329 mW/mg are also observed. These values can be explained by the degradation of UPVC caused by irradiation, elimination of HCl and of H₂, and also by the simultaneous formation of conjugated double bonds phenomena described by the chemical reactions (10) and (11).

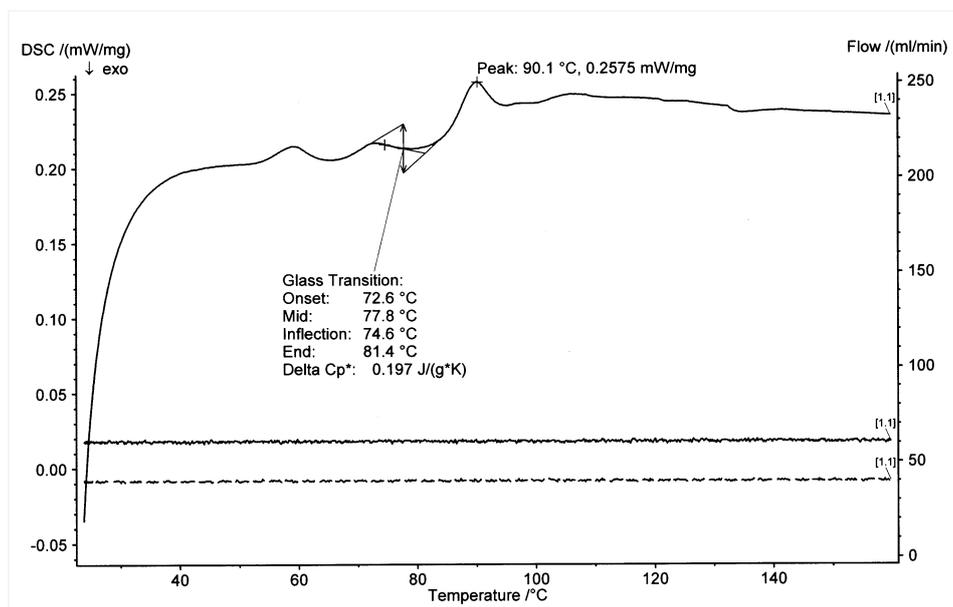


Fig. 5. DSC dependence on temperature (0-160 °C) for UPVC samples irradiated with γ radiations at 16Mrad

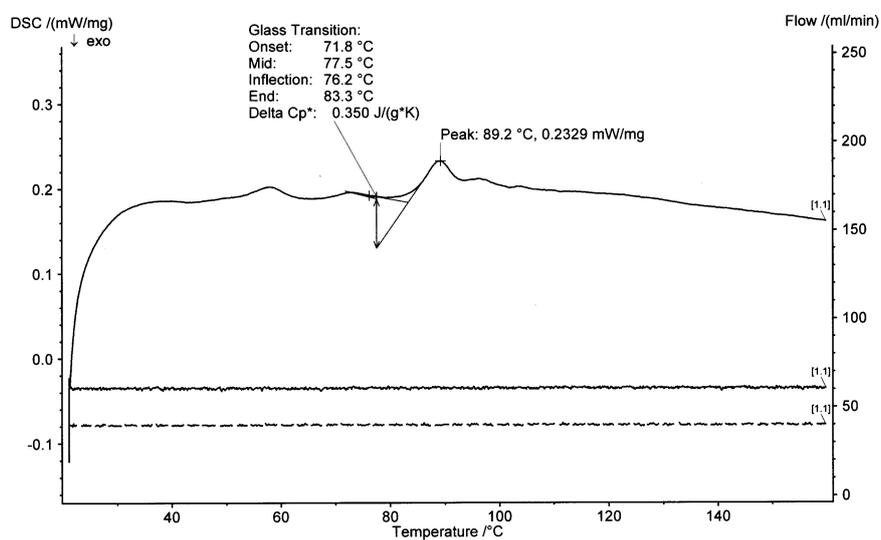


Fig. 6. DSC dependence on temperature (0-160 °C) for UPVC samples irradiated with γ radiations at 50Mrad

In both graphs we notice the appearance of discontinuities and maxima prior to the main peak, attributed to the additives from material. By cooling at zero degrees and a second heating 0-160°C the both graphs present common elements: the disappearance of these maxima due to emission of additives by heating (fig. 7).

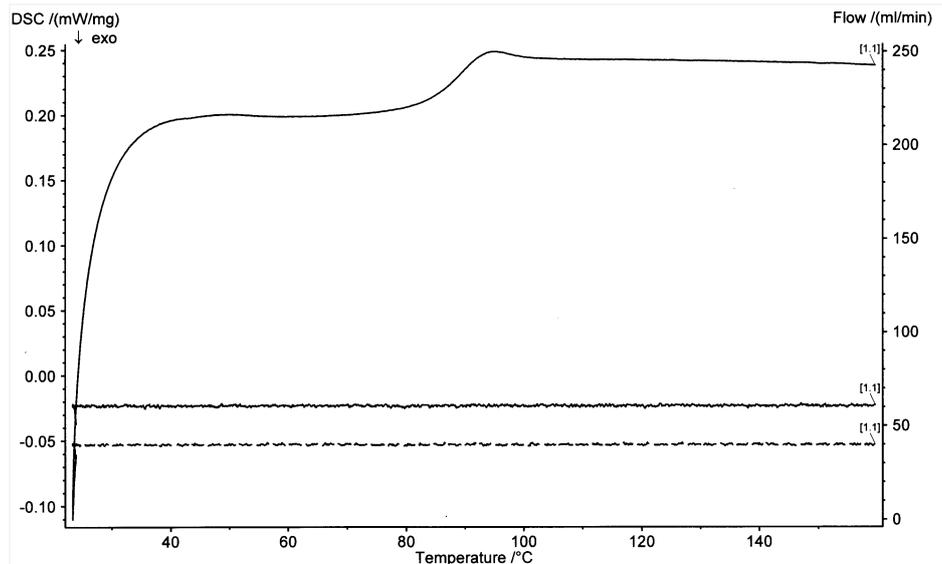


Fig. 7. DSC dependence on temperature after cooling and the second heating at 160°C for UPVC samples irradiated with γ radiations at 50 Mrad

In order to explain the phenomena of degradation we must also take into consideration the oxygen due to irradiation occurring in the air, which leads to the formation of peroxy radicals. These radicals can occur in both crosslinking as well as in the degradation reactions of PVC.

Results obtained at the irradiation γ of UPVC are in agreement with the results from the literature indicating that up to 10 Mrad can be produce in PVC crosslinking processes. Between 1-10 Mrad the damage is considered incipient to mild. From 10-100 Mrad the damage of PVC is considered between mild and moderate. U_p to 100 Mrad the damage is moderate to severe [26].

Conclusions

- Higher level of flexibility, permittivity and losses of insulation and jackets of PPVC for low voltage cables comparatively with UPVC is due to the introduction of additives (particularly phthalates).

-The increase of glass transition temperature T_G and of the domain of glass transition of PPVC by applying a second and third cycle heating/cooling, between (0-160)°C, is due to the emission of additives (phthalates). Phthalates are considered to be among the most universal of all environmental pollutants.

-The glass transition of UPVC is $T_G = 80.6^\circ\text{C}$ (onset 71.1°C and end 81.6°C). The main peak 94.9°C position, energy 0.2118 mW/mg , is attributed to the relaxation phenomena due to the glass transition.

- By applying a second cycle heating/cooling, between (0-160)°C for UPVC, the four peaks which are prior to the main peak 94.9°C (0.2118 mW/mg) disappear. The disappearance is also due to the emission of additives.

- Glass transition for UPVC after the second cycle heating /cooling between (0-160)°C is $T_G = 89.5^\circ\text{C}$ (onset 85°C and end 92.9°C). The growth of T_G can be attributed to the thermal degradation and to emission of additives from UPVC.

- Important increase of T_G for 5.44 Mrad (94.3°C) as compared to the same temperature for 0 Mrad (80.6°C) show that for this dose of radiation (5,44 Mrad) important crosslinking events occur. The presence of crosslinks between chains restricts rotational motion and raises T_G .

- For 5.44 Mrad a significant peak at 113.9°C , with high energy 1.364 mW/mg is observed, indicating a significant increase in relaxation phenomena due to the glass transition and to the crosslinking.

- By increasing the radiation dose from 5.44 Mrad to 16 Mrad and 50 Mrad, respectively, we obtained a decrease of T_G : 77.8°C , and 77.5°C , respectively, which indicates that at these doses there is an increase of the degradation and the scission is more pronounced. The mobility of the main chain also increases.

- The main peaks of relaxation at 16 and 50 Mrad are also observed in the positions 90.1 and 89.2°C . The weak intensities: 0.2575 mW/mg , 0.2329 mW/mg are related with the accentuation of degradation phenomena.

- The phenomena observed are in good accord with the results from literature showing that up to 10 Mrad crosslinking processes can be produced in PVC.

Between 1-10 Mrad the damage is considered incipient to mild. From 10-100 Mrad the damage is considered between mild and moderate.

- The thermal and radiative degradation of UPVC can produce the emission of toxic substances (HCl, toxic additives).

- The exact measurement of glass transition temperature T_G is not easy. T_G depends on a large number of factors that increase or decrease the mobility of the main chain of the polymer.

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