THERMAL EFFECTS OF PVC BY ITS STRUCTURE AND COMPOSITION MODIFICATION

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Owing the possibility of wide modification and price competitiveness in comparison with other polymers, neat poly(vinyl chloride) is used as a base polymer for the creation of various PVC materials, with a huge number of diverse applications. The most valuable are mechanical properties of PVC, its high weather resistance, low thermal conductivity and low flammability, making this polymer preferred for outdoor applications like pipes, fittings, window profiles, windowsills, sewer systems, sheets, panels, films etc. The plasticized PVC is mostly used for manufacturing of electric power cables insulations. The restrictions in processing and applications of this polymer are due to its relatively high glass transition temperature (T_g) and low temperature of degradation.

Temperature depending changes in crystallinity structure

During processing of PVC, a transformation of primary grain morphology into a form of the final product occurs. This process called PVC gelation, is realized by the simultaneously action of heat, pressure and shear, and is generally understood as a breakdown of grains and primary particles followed by formation of a network of crystallites. During gelation the destruction of the original crystalline structures inside the grains and the development of structures with a smaller degree of order, called "secondary crystalline structures" network occurs. The degree of gelation depends on processing parameters and significantly affects the utility properties of the product. Differential Scanning Calorimetry (DSC) is a commonly used technique for the evaluation of PVC gelation, based on the analysis of thermal effects occurring during processing of the PVC grains [1].
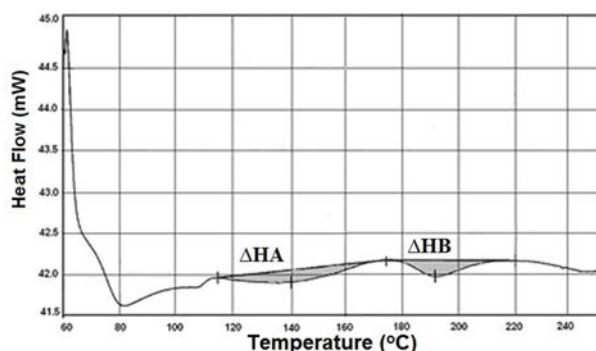

Fig. 1 DSC trace of PVC processed at the temperature of 175ºC,
ΔHA –enthalpy of melting of secondary crystallites,
DHB - enthalpy of melting of primary crystallites

On the DSC run of unplastified PVC samples, processed at selected processing temperature (Fig.1), an endotherm ΔHA related to melting of secondary crystallites appears; the value of ΔHA increases with the processing temperature. The ΔHB endotherm associated with remaining non-

melted primary crystallites decreases and is shifted towards higher temperature. The consequence is the increase of PVC gelation degree, as determined according to the formula proposed by Potente and Schultheis [2]. We have confirmed these effects by DSC measurements performed for PVC processed in a Brabender kneader by temperature 170-200 C (Fig.2).
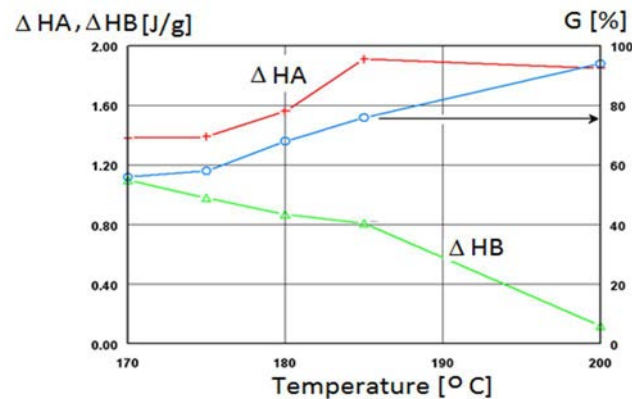

Fig. 2 The values of ΔHA and ΔHB enthalpy and degree
of gelation (G) vs. PVC processing temperature

Nanofiller modified T_g of PVC

It's known that the glass transition might be modified in a wide range by addition of phthalates plasticizers, like diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and di-2-ethylhexyl phthalate (DEHP). The plasticizers commonly lower the temperature of the second-order transition; may lead to reduction of melt viscosity and of elastic modulus, simultaneously improve flexibility and impact strength of the final product [3].

The reason of the relatively high glass transition temperature are strong intermolecular forces between PVC molecules, due to the short distances between them. Introduction of plasticizers causes a swelling of the PVC grains, leading to an increase of distances between polymer macromolecules, followed by the reduction of interactions and, as a consequence, an increase of their mobility. A number of theories explaining the mechanism of plasticizing effect in PVC was developed, including the lubricity theory, the gel theory and the free volume theory [4]. Another modifiers, especially in a form of nanofillers used in PVC compounds, are also leading to changes of T_g. For example the addition of ZnO, Al_2O_3, $CaCO_3$ as well as MMT nanoparticles [5-8] induce an increase of T_g in comparison with the unfilled polymer.

The determination of the value of T_g is usually done not direct, but based on glass transition related effects like changes of electrical and heat conductivity, dielectric constant, specific volume, refractive index, mechanical properties and others. [9]. Thus, the temperature related to the alterations of these properties may be taken as value characteristic for the glass transition. As different effects are usually taken into account, the T_g value vary from one method to another, *i.e.* any of these temperature should be taken as an universal value.

The most often measurement techniques used to determine the value of T_g are differential scanning calorimetry (DSC), thermomechanical analysis (TMA), dielectric analysis (DEA) and dynamic mechanical analysis (DMA) where three typical approaches for calculating T_g by DMA are used: onset of the storage modulus curve, peak of the loss modulus curve and peak of the tanδ curve [10,11]. It has to be stressed that depending on the methods and measurement conditions

used, like various measurement frequency [9,10,12], usually different values of T_g for the same material are detected. These differences are due to various mobility relaxation time of polar groups in the chain, as well as thermal stimulation of macromolecular chains movement. A commonly used DSC method is based on changes in material thermal capacity (Δcp) occurring in the glass transition area, thus the glass transition temperature is the value of the base line deflection, related to alternation of the specific heat [13].

In our research the influence of addition of various nanoadditives i.e. the Si-cage-like structure polyhedral oligomeric silsesquioxanes (POSS), carbon nanofillers like CNT as well as nanosilica on PVC glass transition temperature by DMA, dielectric losses measurements and differential scanning calorimetry [14-16] was investigated. The PVC compound, in a form of dry blend with stabilizer and paraffin wax was applied as a matrix of investigated nanocomposites.

By the investigation of PVC nanocomposites with the MWCNT, independent on measurement method, an increase of T_g with increasing concentration of additive was noted, where the changes of T_g could be observed even for very low nanofiller concentration, signifying an important effect of nanotubes on the PVC chain mobility. We have found that the value of T_g for PVC/CNT nanocomposite is shifted to higher temperature with an increase of the DMA measurement frequency.

The opposite effect *i.e.* lowering of T_g value, independently on the measurement method and frequency, was found in case of PVC modified by POSS with various functional groups (POSS) [15,16]. The T_g dependence on modifier content was determined by DSC and DMTA technique, for measurement frequencies of 1 and 10 Hz. The position of the tan δ at its maximum, as well as maximum value of loss modulus was taken as the glass transition temperature.

In case of PVC modified by a low amount (up to 5 wt%) of POSS with 3-chloropropyl groups (CP-POSS), a decrease of T_g value with increasing modifier concentration, independently on preparation method of PVC/CPOSS samples, as well as on measurement method and frequency, was noted. Moreover, the differences between T_g values obtained from various measurements methods, due to diverse way of stimulation of the chain motions (DSC vs. DMTA) and different time responses of motions, was found [15].

A similar effect appears by modification with the polyhedral oligomeric silsesquioxane containing methacryl and octyl groups on silsesquioxane cage (MeOct-POSS) [16]. In this case any influence of low contain of silsesqioxanes addition (up to 2.5wt %) on the T_g was noticed; a lowering of the glass transition may clearly be seen only by the POSS contain of 5 and 10 wt%. This effect, notably visible by DSC measurement, indicates the tendency of plasticization of PVC by the MeOct-POSS addition, most probably due to the integration of relatively long octyl groups of POSS between the PVC macromolecules. This effect was confirmed in a form of lowering of elastic modulus by uniaxial stress-strain test, particularly for the POSS concentration above 2.5 wt% in PVC matrix. Moreover, independently on type of POSS nano modifier, as higher was the frequency used in our experiment, as higher was the value of the T_g, that is in agreement with results presented for PVC/CNT composites.

Therefore, we have stated that both CP- POSS and MeOct-POSS may be applied as non-phthalate containing plasticizers of the poly(vinyl chloride) [15,16].

The results of DSC tests indicate that the glass transition temperature of poly (vinyl chloride) may also be influenced by modifier with spherical nanoparticles, like nanosilica. The decrease in the T_g value by about 2 % was found when the content of nanosilica in the PVC matrix was 1 wt %. On the contrary, an introduction of 4 and 8 wt% leads to an increase in the glass transition temperature by 5% and 6.5%, respectively, compared to unmodified PVC.

Influence of nanofiller on PVC thermal stability

Another problem by processing of PVC is its low thermal stability. Depending on the PVC processing methods and application of products, different types of stabilizers are used. These stabilizers are introduced either individually or more often in a form of systems of composition that causes a stabilizing synergic effect. Beside the standard stabilizers, an enhance of PVC thermal stability by other additives, including fillers in PVC compounds like hydrotalcite, modified MMT, kaolinite, nanoparticles $CaCO_3$ was described in the literature [16-19]. In our investigations we have confirmed a valuable effect of 1 wt% nanosilica particles introduced to PVC matrix by rolling mill method. Based on congo-red measurements, thermal gravimetric analysis and by visualization of color changes of PVC processed at various rolling time we have found a beneficial influence of nanosilica on the PVC thermal stability, used as a matrix of the nanocomposites.

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