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Kinetics of decomposition of poly(vinyl chloride)/low-migration polyesterurethane plasticizer blend — a thermogravimetric study

RAPID COMMUNICATION

Summary — Kinetics of decomposition of poly(vinyl chloride) (PVC), plasticized either by di(2-ethylhexyl)phthalate (DEHP) or medium molecular weight polyesterurethane (PESTUR) or by both plasticizers, was studied by isoconversional methods on the basis of thermogravimetric data under dynamic heating conditions. It has been found that the initial decomposition temperature is higher for PVC plasticized with PESTUR in comparison with PVC plasticized with DEHP or with PESTUR/DEHP, and thermal degradation shows features of multistep complex process. Application of polymeric plasticizer leads to the increase in values and a "smoothing" effect in the course of energy of activation and pre-exponential factor at initial stage of decomposition indicating thus the hindered migration of medium molecular weight compound from PVC matrix (in comparison with PVC containing monomeric DEHP) due to steric hindrances as well as due to specific interactions between C=O and Cl groups along the macrochains.

Key words: poly(vinyl chloride), polymeric plasticizer, kinetics of degradation, energy of activation, thermogravimetric analysis.

Plasticized poly(vinyl chloride) (PVC) is one of the most widely used polymeric materials for medical applications. Flexible PVC is used for the manufacture of blood bags, transfusion tubings and as packaging for pharmaceuticals [1, 2]. PVC used in medical applications contains up to 40 % (by weight) of the plasticizer which is usually di(2-ethylhexyl)phthalate (DEHP). However, DEHP is a hypolipidemic hepatocarcinogen and there are some reports questioning the safety of DEHP in PVC-based medical devices [3—6].

Generally, the subject of migration and volatilization of plasticizers has been widely studied [7—10]. Hence, various attempts have been made to reduce plasticizer migration from plasticized PVC; methods employed include coating of PVC surface with polymers such as acrylates or polyesters, crosslinking of PVC during processing with peroxides or grafting hydrophilic monomers onto the surface of PVC by γ-radiation/plasma treatment [11, 12]. PVC was also chemically surface modified by nucleophilic substitution of chlorine atoms by photoactive *N,N*-diethyl dithiocarbamate in aqueous media in the presence of a suitable phase transfer catalyst — further crosslinking by irradiation with UV resulted in formation of a barrier for the diffusion of DEHP from the matrix [13]. One of the recent research directions towards lowering the migration and volatilization of plasticizers from PVC is application of high molecular weight elastomeric polymers *e.g.* polyester-based thermoplastic polyurethane (TPUR) elastomers as blending resins that display plasticizers' performance. Unfortunately, PVC/TPUR blends are difficult to process due to their high melt viscosity and limited heat stability [14—16]. These drawbacks could be at least partially eliminated if medium molecular weight semi-solid OH-terminated polyesterurethanes (PESTUR), showing high degree of compatibility with PVC matrix, were for plastification purposes [17—19].

Hence, in this communication some kinetics aspects of the degradation process of PVC plasticized with novel macromolecular polyesterurethane-based plasticizer are reported.

EXPERIMENTAL

Materials

Suspension PVC (K-70) was a product of ANWIL SA, Włocławek (Poland).

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As monomeric plasticizer di(2-ethylhexyl)phthalate (DEHP) produced by Boryszew SA Sochaczew (Poland) was used.

Polyesterurethane (PESTUR) of M_w = 13 000 was synthesized at Industrial Chemistry Research Institute by prepolymer method using isophorone diisocyanate and a copolymer of 1,6-hexanediol and adipic/phthalic acid.

Preparation of samples

PVC compositions were prepared in a two stage process; during the first stage, dry blends of PVC and additives were obtained in a high-speed mixer at 100 °C and then the blends homogenized at 160 °C in a Brabender Plasti-Corder were processed in a laboratory Brabender single-screw extruder at 155—165 °C. Finally, square plates were press molded at 165 °C under 7 MPa pressure. The detailed description of this procedure was presented elsewhere [17].

Table 1. Description of the samples of PVC plasticized with different plasticizers

Symbol of sample	Plasticizer (amount in wt. %)
1	DEHP (33.5)
2	DEHP (18.5)/PESTUR (15)
3	PESTUR (50)

Description of the samples is given in Table 1.

Method

Thermogravimetric analysis (TGA) was performed using a Netzsch TG 209 thermal analyzer in argon atmosphere using open α-Al_2O_3 pan, operating in a dynamic mode at a heating rate 2.5, 5, 10 or 20 K/min. The sample weight was about 7 mg.

RESULTS AND DISCUSSION

At the first stage, analysis was performed at heating rate of 10 K/min to ascertain the thermal stability of the samples — results are shown in Fig. 1.

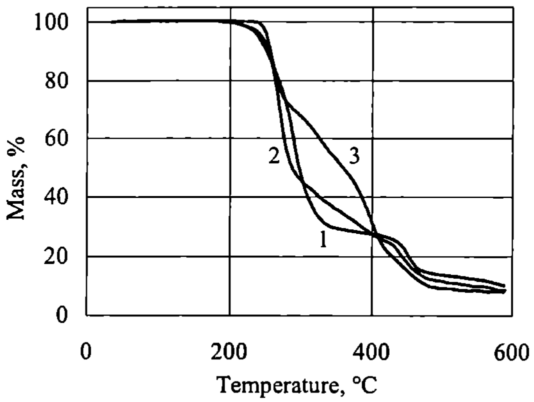

Fig. 1. TGA profiles of samples 1—3 obtained at heating rate 10 K/min

It can be seen that the initial decomposition temperature of sample 3 is the highest, reaching 252 °C, whereby for samples 1 and 2 it is 215 and 225 °C, respectively. Degradation shows features of a multistep complex process. To obtain additional information of the nature of this process a kinetic analysis was performed by two isoconversional methods (by Ozawa—Flynn—Wall and Friedman) that yield values of activation energy (*E*) and pre-exponential factor (*A*) [20—22]. Both methods lead to similar results.

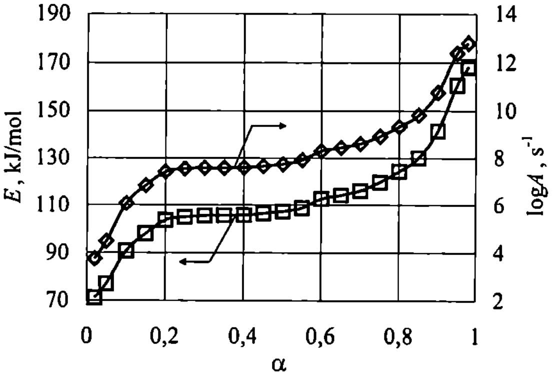

Fig. 2. Energy of activation (E) and logarithm of pre-exponential factor (A) versus fractional mass loss (α) for the degradation process of sample 1 calculated by Ozawa—Flynn—Wall method

The results of Ozawa—Flynn—Wall analysis of the thermal degradation of sample 1 are presented in Fig. 2. *E* and *A* are plotted versus fractional mass loss (α), what is a measure of conversion degree. There are three regions of energy of activation and pre-exponential factor changeability which arise from migration of the monomeric plasticizer and decomposition of PVC matrix.

The first region is most likely associated with migration of plasticizer which is lost first from the surface and then from the bulk. Murase *et. al.* [23] also investigated the migration of DEHP in PVC under heating by depth analysis but using FT-IR spectroscopy and noticed that depth profiles depended on the stabilizers used. For PVC/DEHP stabilized with di-*n*-butyl-tin-dilaurate, DEHP seems to be lost first from the surface, and then diffuses from the polymer matrix to the surface, which is a typical pattern of diffusion control. On the other hand, in PVC/DEHP containing di-*n*-butyl-tin-dilaurate or di-*n*-butyl-tin-maleate polymer DEHP evolution is less intensive and characterized by a smaller rate coefficient — this is a typical surface control pattern [23].

Isothermal weight loss kinetics of plasticized PVC at the temperature range 85—120 °C, studied by Audouin *et. al.* [24], showed that in this temperature range the plasticizer loss was the only significant source of weight change, but still at least two different kinetics regimes were involved, as evidenced by the characteristic shape of Arrhenius plot. It could be supposed that almost continuous plasticizer monolayer existed at the sample surface, making the evaporation rate practically insensitive to the plasticizer bulk concentration. Indeed, when this latter decreases, the free volume fraction and thus, the plasticizer diffusivity decreases and can reach a critical value beyond which the whole process becomes diffusion-controlled. A simple kinetic model cannot, therefore, describe the whole plasticizer-loss process since there is probably a kinetic transition stage between the two regimes.

At higher temperature a gradual decomposition of the PVC matrix takes place by splitting off hydrogen chloride. As earlier investigations showed, during this process polyene sequences were formed that were active in secondary reactions leading to crosslinking and formation of aromatic pyrolysates [25, 26].

Kinetic analysis by Friedman method of degradation of sample 2 shown in Fig. 3 leads to conclusion that the addition of PESTUR as polymeric plasticizer causes an increase in values and "smoothing" of a curve of activation energy and pre-exponential factor versus degree of conversion profile (up to $\alpha < 0.7$).

As it was shown in Fig. 4, the use of only PESTUR as a plasticizer in amount 50 wt. % (sample 3) makes the thermal decomposition characterized by relatively stable E and A profile, apart from the final stage for $\alpha > 0.8$.

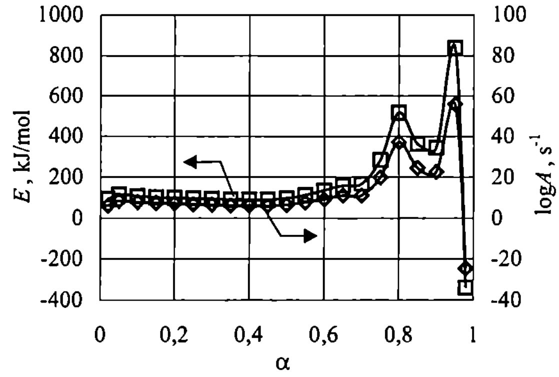

Fig. 3. Energy of activation (E) and logarithm of pre-exponential factor (A) versus fractional mass loss (α) for the degradation process of sample 2 calculated by Friedman method

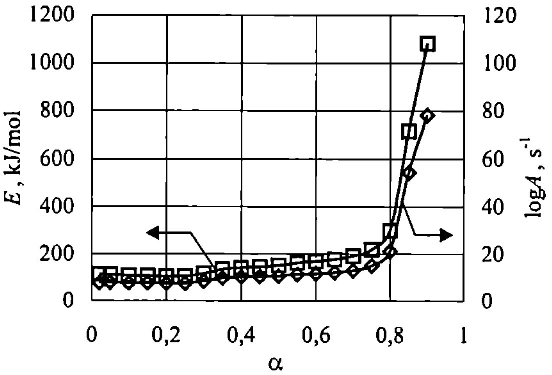

Fig. 4. Energy of activation (E) and logarithm of pre-exponential factor (A) versus fractional mass loss (α) for the degradation process of sample 3 calculated by Ozawa-Flynn-Wall method

The different kinetic behaviour of PVC plasticized with PESTUR in comparison with PVC containing monomeric DEHP can be explained in terms of hindered migration of medium molecular weight compound from PVC matrix due to steric hindrances as well as due to specific interactions between C=O and Cl groups along the macrochains. It is well known that chlorinated polymers are miscible with many polyesters and it has been shown that the miscibility of these blends can be due to hydrogen bonding between the C=O groups of the PESTUR and α-hydrogen of chlorinated polymer [27, 28] or C=O¨Cl-C interactions of dipole-dipole type [29, 30]. By the appropriate arrangement of Cl atoms in the polymer structure, the latter interaction will become a factor controlling the properties of the blend. This will occur as the greater the number of non-repulsive interactions which exist on a molecular level between the blend's components, the more dense the arrangement of the microstructure leading to an improvement in the system's physical properties. On the other hand, the rate of diffusion of volatile products through microphase domain structure may differ due to changes in morphology arrangement thus considerably affecting the overall decomposition route.

Moreover, the complete morphological and structural description of PVC/PESTUR blend is extremely complex since both PVC, with its hierarchical microstructural arrangement, and PESTUR, containing alternate soft and hard segment units, contribute to the multicomponent blend system thus affecting considerably its thermal properties.

Further kinetic studies towards determination of the form of f(α) model functions are underway and will be reported in the future [31].

CONCLUSIONS

It has been found that the application of polyesterurethane plasticizer led to the increase and a "smoothing" effect in the course of activation energy and pre-exponential factor at the initial stage of PVC blends degradation indicating thus the hindered migration of medium molecular weight compound from PVC matrix (in comparison with PVC containing monomeric DEHP) due to steric hindrances as well as due to specific interactions between C=O and Cl groups along the macrochains. Hindered migration of a plasticizer is an extremely important parameter in medical applications, so the results obtained may be applied to design of PVC blends with improved properties.

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