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Dehydrochlorination of PVC Compositions During Thermal Degradation

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Abstract

The polyvinylchloride (PVC) differs from other polymer materials by low thermostability. The process of dehydrochlorination takes place even at low temperatures. The purpose of this investigation was to determine the influence of different PVC additives on formation of hydrogen chloride (HCl) from thermal degradation in different gaseous fluids. It has been established that the HCl formation takes place more in nitrogen as a medium than in air medium at a given temperature, especially for the high temperature region. Dibutyl phthalate (as a plasticizer) in 25 mass % w.r.t. PVC, reduces the mass loss due to HCl formation by about 5%, which is the result of two interaction processes - between HCl and plastifier degradation products. It has been found that the addition of 5 mass % of stabilizer in PVC slows down the process of dehydrochlorination and as a result the loss of mass is 2-5% less, compared to non-stabilized samples. Calcium carbonate as a filler was found to be active above 400-500°C and reduction in mass loss was found to be up to 15% at a temperature range of 800-900°C. Calculation of kinetic parameters shows that the rate of dehydrochlorination depends on the composition of PVC. The activation energy of formation of HCl in air, in a temperature range of 400-600°C has been found to be 12.7, 13.3, 16.1 kJ/mol for pure, plasticized and stabilized PVC, respectively. The results reported here shall be useful for development of methods for waste utilization and their influence on the environment.

Introduction

The amount of plastics produced increases every year, the majority of commodity plastics being polyethylene, polypropylene, PVC and polystyrene. In terms of the quantity of production, PVC occupies second position, next to polyethylene [1]. The world production of PVC was 25 million tones in 1998, of which, 5 million tones were produced in Western Europe [2]. It is projected that by 2002, the world and Europe production of PVC will reach 35 and 7 million tones respectively. About 50% of PVC production goes into building, 30% for packaging materials, 8% for electronics, 9% for transportation and 3% for other uses [3]. Of the total quantity of waste generated currently, plastics account for 8% and the contribution of PVC is 15% [4]. PVC doesn't burn, it is a good dielectric, possesses good characteristics. Yet, the production of PVC and its waste utilization has a major impact on the environment. About 88 organic compounds have been identified in the air from working zones, where PVC products are manufactured by the method of extrusion. About 67 of those organic compounds have been identified to be hydrocarbons, 14 oxygen-containing compounds and 6 chlorine containing compounds [5]. About 170 compounds have been identified during the burning of PVC products, some of which possess carcinogenic and mutagenic properties [6]. It is evident that the composition of the PVC compounds has a significant contribution on its thermal degradation process and hence on the volatile organic compounds generated.

Experimental

PVC powder produced by the French company ATOchem with an average molecular weight of 255,000 and polydispersity of 1.77 has been used in our investigation. The PVC compound consists of 25 mass% of dibutyl phthalate as plastifier, 5 mass % of

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*corresponding author. E-mail: abadie@univ-montp2.fr lead dioxide as stabilizer and 25 mass % of calcium carbonate as filler. The purpose of this work was to study the influence of the above mentioned additives on the formation of decomposition products during its thermal treatment in air and nitrogen.

The experiments were carried out in an experimental installation, consisting of a pipe-still heater, with a range of heating temperature up to 1,200°C, supplying gas (air, nitrogen) (Fig. 1). Temperature inside the furnace was controlled by the chromel-alumel thermocouple, attached to a millivoltmeter. The samples of PVC were put in a charging apparatus, made from the thermally stable ceramic material. Air at a flow rate of 300 ml/min., was used as a medium inside the heater, while nitrogen was used for oxygen-free medium. The HCl formed during thermal degradation was absorbed into water, which was quantitatively measured using potentiometry. The materials used in the experimental installation were neither reactive with HCl nor had any affinity to absorb the gas liberated. The error during absolute pH measurement using Ionomizer was about 0.01%.

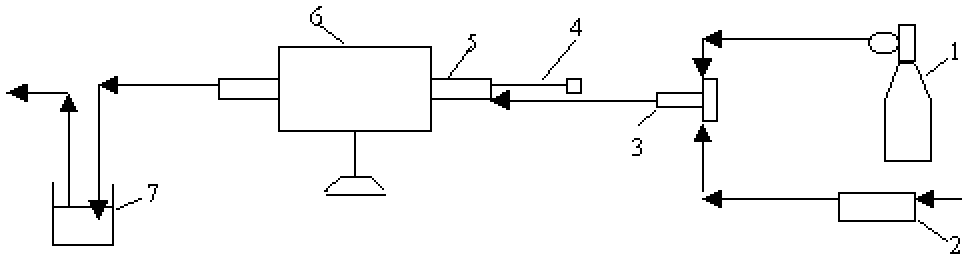

Fig. 1. Experimental installation. 1-container with nitrogen, 2-microprocessor, 3-tap, 4-sliding equipment, 5-quartz tube, 6-furnace, 7-absorbing bottle (dosimeter of chromatograph).

The heating rate during the course of thermogravimetric analysis was 10°C/min., with an experimental error of about 0.01 mass %. Gas Chromatography with the built-in dynamic pyrrolitic alveole was applied for the chromatographic studies, with flame ionization detector (FID). The sample has been kept in the furnace at the constant temperature for the period, sufficient for complete destruction. The samples of polymers with mass 30-40 g were used during investigation of thermal degradation processes of PVC.

Thermal degradation of pure PVC

Some relationships which are presented in Fig. 2 and in Fig. 3. have been found while studying the HCl formation as a result of thermal degradation of pure PVC and that with different additives, both in the air and nitrogen.

The data from literature confirm that there is acceleration in the process of PVC degradation in presence of air [7]. In the nitrogen medium the formation of HCl starts at lower temperature (285°C) than compared to air (319°C) [8]. The evolution of HCl takes place in a narrow interval of temperature, with nitrogen as the medium. In the nitrogen medium dehydrochlorination is generally completed at temperatures, at which the polymer chains have not faced sufficient changes and the probability of interaction between HCl and additives is small. In the air medium, dehydrochlorination is completed at higher temperatures and the HCl formation can be accompanied by the degradation of polymer chains and interaction between HCl and additives. Therefore, yield of HCl is more completed in the nitrogen medium

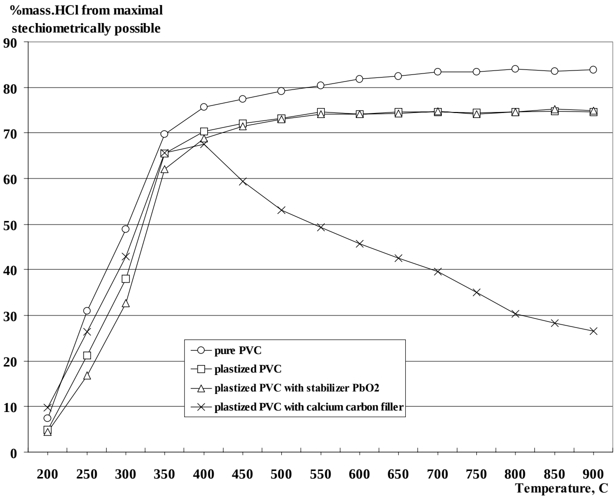

Fig. 2. HCl formation during the thermal degradation of PVC containing different additives, in air.

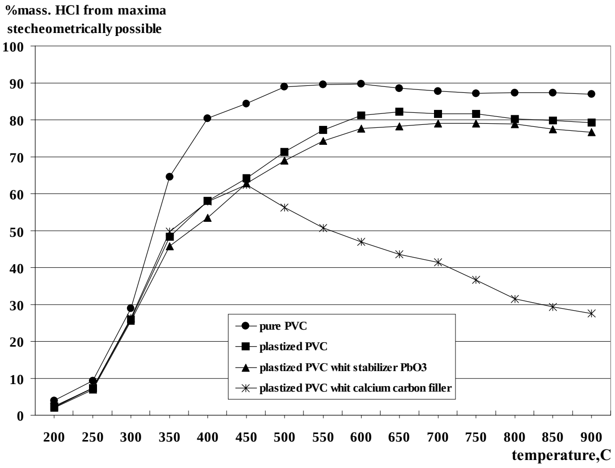

Fig. 3. HCl formation during the thermal degradation of PVC containing different additives, in nitrogen.

than in the oxygen medium.

The higher amount of HCl formation in the nitrogen medium is probably determined by more complete degradation of the terminal chains. In case of air as compared to nitrogen, part of the chlorine (about 25% of the maximum possible) can remains in the residual units [9]. The amount of residual units of degraded PVC in nitrogen is lower, which accounts for the near completion of HCL formation in air. The fact that there is no significant amount of HCl liberated at a temperature of 600°C probably indicates that there is some sort of reaction taking place between HCl and the unsaturated hydrocarbons formed. This has been confirmed from the results of chromatographic analysis of pyrolytic degradation products of PVC. Above 600°C, the formation of benzyl chloride is increasingly observed [10]. The pyrolysis gaseous products also contain sufficient quantity of unsaturated hydrocarbons - ethylene, propylene, vinyl chloride, benzene vinyl, which can react with HCl by addition reaction [11].

The results of thermogravimetric and chromatographic analysis in air show that the major mass loss corresponds to the emission of HCl, during the temperature interval of 240-380°C. During this interval, the mass loss of the PVC sample is about 64% of its original mass (Fig. 4). The first peak (TR1) corresponds to HCl, whereas the second peak (TR2) corresponds to hydrocarbon like degradation products.

According to the results from chromatographic data, there is also the formation of vinyl chloride, methane, ethylene, carbon dioxide and other byproducts formed along with HCl during the pyrolysis of PVC.

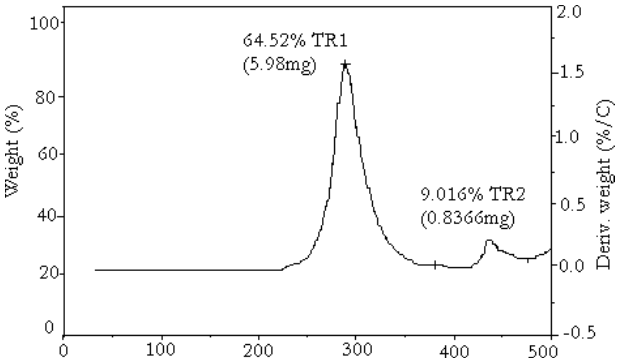

Fig. 4. Themogravimetric analysis of pure PVC.

Thermal degradation of plasticized PVC

It can be assumed that the addition of plasticizers to a polymer sample will have influence on the dehydrochlorination's process, because of the interaction between HCl and other degradation products with the plasticizer molecules. During the degradation of PVC in the air, the formation of HCl is slower from the plasticized PVC, as compared to the virgin polymer. The plasticizer seems to degrade and comes out from the polymer earlier than the degradation of the polymer itself, thus coinciding with HCl formation in the temporary interval. Part of the energy requirement can be spent on the degradation of the plasticizer. Therefore, at equal temperatures, the plasticized PVC samples give less hydrogen chloride than pure PVC. The plasticizer acts as a kind of inhibitor for the formation of HCl, although the plasticized sample starts to degrade earlier because of the degradation of the plasticizer. At elevated temperatures, the difference in the quanity of HCl emitted for the plasticized and unplasticized PVC samples reaches a 5 mass % (Fig. 2).

The products of PVC degradation, both unsaturated and saturated hydrocarbons, produce chlorinated hydrocarbons while coming in contact with HCl. The first two peaks from the degradation of plasticized PVC (TR1 and TR2) correspond to the degradation of the plasticizer whereas the third peak (TR3) corresponds to the formation of HCl and the forth peak (TR4) corresponds to hydrocarbon like degradation products (Fig. 5).

It has been shown by chromatographic analysis, that the degradation products from plasticized PVC contain decomposition products such as dibutyl phthalate, butane, butyl aldehyde, butyl alcohol, phthalic anhydride, which are not typical of pure PVC. Also found is a significant quantity of butyl chloride (up

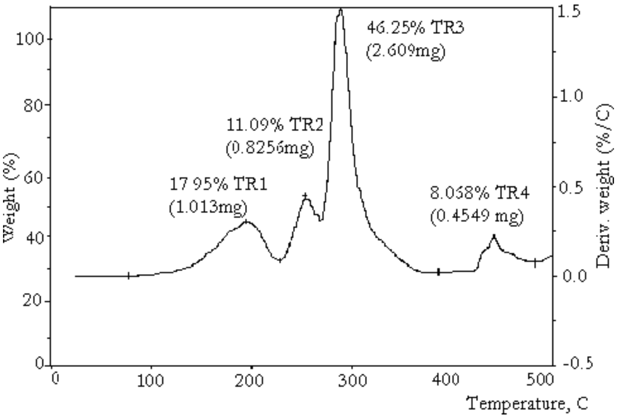

Fig. 5. Thermogravimetric analysis of plasticized PVC.

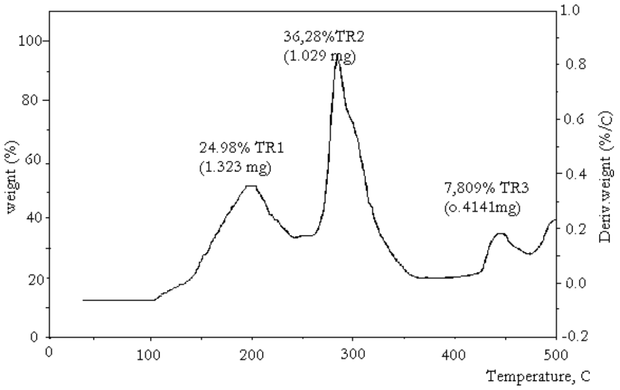

Fig. 6. Thermogravimetric analysis of PVC with calcium carbonate as filler.

to 2.5 mass %), as well as methyl-, ethyl-, and vinylchlorides.

Thermal degradation of PVC containing filler

It is possible to assume that the calcium carbonate as additive in the amount of 25% should essentially reduce the quantity of hydrogen chloride formed at the thermal degradation of PVC, resulting from the following reaction:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

The effects of fillers on the thermal degradation of PVC results are represented in Fig. 2 and Fig. 3. The decrease of the HCl formation is observed at temperatures higher than 350°C in air, whereas the same for nitrogen as the medium occurs at temperatures higher than 450°C. The highest amount of mass loss as a result of dehydrochlornation was 15 mass %, which occurs at temperature of 900°C and above. Thermogravimetric data has established that there is interaction taking place between calcium carbonate, plasticizer and HCl (Fig. 6). The peak in the range of temperatures 250-280°C (TR2, Fig. 5) corresponds to dibutyl phthalate decomposition. It can be assumed that the absence of this peak in Fig. 6 may show a possible interaction between dibutyl phthalate degradation products and calcium carbonate.

Thermal degradation of stabilized PVC

It is known [6] that HCl catalyzes the process of PVC dehydrochlorination. Therefore, the action of some stabilizers, added to the polivinylchloride can neutralize the deleterious effect of the negligible amount of HCl formed during the initial stages of the heat treatment process.

While studying the influence of the stabilizer at 5 mass %, it was discovered that the presence of the stabilizer reduces the HCl formation compared to unstabilized PVC by about 2-5 mass % (Fig. 2 and Fig. 3).

Results from gas chromatography show that the addition of lead oxide helps in the formation of branched hydrocarbons in products [10]. It has been recognized that the addition of lead oxide results in the formation of high molecular weight polyaromatic hydrocarbons, which are relatively non-volatile.

The process of dehydroclorination is a function of time, the medium (nitrogen or air) of reaction, formulation of the PVC compound(s) as well as the heating rate. Therefore, the kinetic study of such a process, which is useful for development of waste utilization, is immensely important. The kinetic information for the formation of HCl has been obtained under different conditions. It has been observed that the reaction follows a first order. Calculation of activation energy was done from the plot of lnK vs 1/T, as described in the literature [12]. The values of activation energy for the dehydrochlorination in air for stabilized, plasticized and virgin PVC, in a temperature range of 400-600°C has been found to be 16.1, 13.3 and 12.7 kJ/mol respectively. The additives do result in a slow down in the rate of formation of HCl as well as a reduction in the weight loss of PVC from the process of dehydrochlorination.

Conclusion

We have determined the influence of different PVC additives on formation of hydrogen chloride (HCl) from thermal degradation in different gaseous fluids. It has been established that the HCl formation takes place more in nitrogen as a medium than in air medium at a given temperature, especially for the high temperature region. Dibutyl phthalate (as a plasticizer) in 25 mass % w.r.t. PVC, reduces the mass loss due to HCl formation by about 5%, which is the result of two interaction processes - between HCl and plastifier degradation products. It has been found that the addition of 5 mass % of stabilizer in PVC slows down the process of dehydrochlorination and as a result the loss of mass is 2-5% less, compared to non-stabilized samples. Calcium carbonate as a filler was found to be active above 400-500°C and reduction in mass loss was found to be up to 15% at a temperature range of 800-900°C. Calculation of kinetic parameters shows that the rate of dehydrochlorination depends on the composition of PVC. The activation energy of formation of HCl in air, in a temperature range of 400-600°C has been found to be 12.7, 13.3 and 16.1 kJ/mol for pure, plasticized and stabilized PVC, respectively. These results should be useful for development of methods for waste utilization and their influence on the environment.

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