

Thermodestruction in the Surface Layer of Poly(vinyl chloride) During Extrusion

Vitali T. Lipik,¹ Marc J. M. Abadie,¹ Nikolay R. Prokoptchuk²

¹Laboratory of Polymer Science and Advanced Organic Materials LEMP/MAO, University Montpellier II, Science and Technology of Languedoc, Place Eugène Bataillon, 34095 Montpellier Cedex 05, France

²Department of Petrochemical Synthesis Technologies and Processing of Polymeric Materials, Technological State University of Belarus, Sverdlova str. 13-a. 220050 Minsk, Belarus

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ABSTRACT: Polymeric raw material passing through the extrusion machine and other forming devices undergoes the processes of destruction, which result in the formation of potentially harmful substances and their accumulation in the surface layers of the product directly contacting with heated parts of forming machines. The research of the top layer of a poly(vinyl chloride) profile has shown that the surface layer of polymer contains a number of chlorinated hydrocarbons. The following substances have been identified during the research of the hydrocarbons composition contained of the surface layer: hexachlorobenzene, hexachlorobutene, chloroform, acetyl chloride, bi-

phenyl, anthracene, naphthalene, and other hydrocarbons. The difference of calculated activation energy of thermooxidizing destruction of surface and internal layers of a polymeric product reveals the process of partial destruction of a surface layer. Data about semivolatile substances, concentrating in polymer surface during processing will be used for development of stabilizers, ecology, and polymer-manufacturing techniques. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2076–2080, 2008

Key words: degradation; poly(vinyl chloride); extrusion; activation energy; chromatography

INTRODUCTION

The estimation of polymer life cycle influence on the environment has great value for ecology, sanitary, hygiene, machinery, and technology. The usage stage remains the least investigated when compared with other stages of polymer life cycle, while the emission of potentially harmful substances emitted from polymer is extremely small and stretched out in time. It is difficult to estimate the overall emission of all harmful substances from polymer. Therefore, it is of interest to research the nonvolatile and semivolatile substances contained in the polymer, which potentially evolve during the use of a product and determine the emission structure.

Poly(vinyl chloride) (PVC) is one of the most widely distributed polymeric materials in day-to-day life. Owing to the active usage of PVC for manufacturing of construction finishing materials, people are in direct contact with this polymer. About 50% of PVC made worldwide in 2000 was used in products for construction (windows, doors, laminated floors, internal and external siding, profiles, furniture accessories, etc.).¹ In the year 1996, 90% of all wallpaper manufactured in Japan were made of PVC. About 74% of all polymeric

pipes are made of PVC.² A lot of attention is paid to the process of harmful substances evolution during burning and pyrolysis of the polymer itself, whereas the extent of emission during the production and usage of PVC has received scant attention for scientific investigation. The depth of PVC destruction process, the mechanism of thermooxidizing destruction of material under influence of forming equipment, and furthermore, the substances accumulated in the material during processing are not adequately investigated. It is possible to assume that the surface of a polymer product is exposed to contact with the extruder and other heated up equipment, therefore it contains the greatest amount of destruction products. It is possible to define the total amount of destruction product contained in polymer by means of polymer example dissolution.³ But the emission from polymer during the usage stage is mainly defined by the substances that are kept on polymer surface or contained in polymeric matrix, which is immediately close to the surface. Chlorinated hydrocarbons represent special interest in PVC thermodestruction, because they provide major danger of emissions.

PVC can be characterized as rather unstable material at heating and it is one of the less stable carbon chain polymers.⁴ The problem that the PVC products manufacturers have to live with is the fact that the polymer starts degrading already at the processing stage. To prevent PVC destruction upon processing stage,

Correspondence to: V. T. Lipik (lipikv@yahoo.com).

various stabilizers are added to the polymer. However, thermal oxidation still occurs during PVC extrusion and it is possible to evaluate the degradation extent by measuring the emission of various substances in atmosphere surrounding the working area.

The objective of this investigation is to examine the surface layer (up to 0.1 mm) of PVC profile and layers situated beneath it. The aim of our work is to prove the occurrence of polymer surface destruction during extrusion process. Another aim is to get information on the composition of the semivolatiles compounds accumulated on the surface layer during PVC extrusion. This point could be of interest in evaluation of the harmful potential of PVC items during their exploitation.

EXPERIMENTAL

Materials and equipment

Poly(vinyl chloride) (PVC) siding and window profile manufactured by Rehau (Germany) and Becker-system (Belarus) and not plasticized were used during this research. Methylene chloride 99.9+%, supplied by Aldrich (France) and sodium chloride 99.8% from Prolabo (France) were used without any treatment. Anthracene D-10 98+ atom% D was bought from Akros Chemicals (France).

The activation energy of polymer weight loss, according to the data of dynamic thermogravimetry, was determined by Broido's method⁵ for surface and internal layers of polymer. Q-1500 D (MOM Budapest) has been used under the following conditions: weight scale, 200 mg; heating rate, 5°C/min; range of temperatures 20–500°C. Two hundred milligrams of polymer were taken from the surface (0.1 mm) and 200 mg from the inside layers (on a fresh cut) of each kind of PVC profile for thermogravimetric analysis. The simple average of three experiments was accepted as the result. The percent loss of sample weight to within 0.1% (heating rate 10°C/min) was graphically determined on the derivatogram for the degradation of the material inside. The value of activation energy of thermooxidative destruction [*E*] has been calculated (to within 1 kJ) according to the eq. (1)⁵:

$$\ln \left[\ln \left(\frac{100}{100 - \Delta m} \right) \right] = -\frac{E}{R} \frac{1}{T} + \text{const} \quad (1)$$

Activation energy was found from the slope of the plot $\ln [\ln (100/100 - \Delta m)]$ vs. $10^3/T$ (K) [eq. (2)]:

$$[E] = R \text{ tg } \varphi \quad (2)$$

where *R* is the universal gas constant equal to 8.31×10^{-3} kJ/mol °C, and φ is the slope.

Research of PVC emissions composition was carried out on HEWLETT PACKARD HP 6890 SERIES GC

System chromatomass-spectrometer with a 25 m long, 0.25 mm diameter capillary column, with stationary phase HP-5MS (crosslinked 5% PH ME Siloxane). The thermostat temperature of column was increased from 40 to 300°C with a speed of 5°C/min, during the analysis. Helium with flow rate of 1 L/min was used as carrier gas. The temperature of injection was 320°C. The injection volume was 2 μL. A PVC-free control sample has been injected. The quantity of emitted substances was estimated by the internal standard method where the anthracene *d*-10 with concentration of 2 μg/L was used as the standard.

The quantity of hydrogen chloride emitted from the samples and absorbed during the experiment was determined by a potentiometric method, by means of chlorine-selective electrode. Absolute chloride calibration has been performed using sodium chloride solutions. Potentiometric method with universal ionomer EV-74 (Gomel, Belarus) was used for the measurement of chloride ions concentration in samples. An allowable basic error of the device is 2.2 mV at a range of measurements 1–5 pC_{Cl} (pC_{Cl} = $-\log (C_{Cl^-})$). Additional error in a circuit of the auxiliary electrode is 0.25 mV at every 10 kΩ, and in a circuit of the measuring electrode –0.25 mV at every 500 MΩ. A membrane chlorine selective electrode (Tbilisi, Georgia) with linearity of measurement in the range 1.1–10 pH and a glass auxiliary electrode (Gomel, Belarus) with maximal deviation of measurements, no more than 0.2 pH units, were used for chloride ion measurement. The temperature of each measurement was 20–22°C. The time of each measurement was 3 min.

Degradation procedure

Heating and purging by air of PVC sample were conducted to cause migration of substances contained in a polymer surface. PVC samples of about 40 g in weight and a surface area of 300 cm² were put in a glass vessel mounted on a water bath and were maintained for 3 h at a purge of the vessel by air with a flow rate of 1 L/min. The blown air passed through a porous lining of an absorbing vessel, and the volatile chlorine-containing compounds were absorbed by methylene chloride. The evaporating solvent was condensed in a reflux condenser. The quantity of solvent had been set to 1 mL by the evaporation before the analysis. The temperatures of water bath were 50 and 100°C.

The surface layer of polymer with thickness of 0.1 mm was eliminated by a mill from the second sample of PVC profile similar in weight and surface to the first one. The second sample was exposed to the similar procedure of keeping on a water bath in a vessel with absorption of emitted substances by methylene chloride. One control experiment was made with a purge of an empty glass vessel without a PVC sample and passage of the air through the methylene chloride

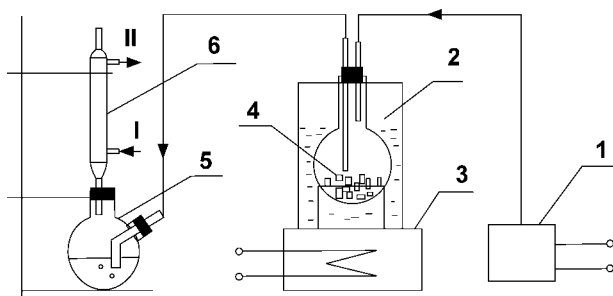


Figure 1 Experimental installation, I and II: input and output of cooling water, (1) blower, (2) water bath, (3) electric heating device, (4) PVC sample, (5) absorbing vessel with methylene chloride, and (6) condenser.

solution. Results of the given experiment were used for quality assurance to exclude influence of the equipment. Each kind of experiments was carried out three times with the subsequent averaging of the results. The layout of the experimental installation is shown in Figure 1.

RESULTS AND DISCUSSION

Data about composition of volatile substances of PVC destruction during extrusion have been previously investigated and studied.⁶ However, hardening polymeric matrix at the extruder exit keep part of semivolatile and nonvolatile destruction products. Since the PVC surface layer comes in direct contact with the equipment parts, it supposedly should contain the greatest amount of thermodestruction products.

Thus, these facts were preconditions while investigating the surface layer of PVC products. The activation energy of PVC thermodestruction was determined with the help of thermogravimetry for the purpose of general estimation of thermodestruction processes of surface and deep polymer layers, which were exposed to heating during extrusion processing. Data on calculation of activation energy of a PVC sample taken from the top and from the internal part of the material are given in Table I.

Lower activation energy on the surface of polymer products indicates higher volatility due to the reduction of molecular weight, occurrence of nonsaturated bonds, oxidized areas, and course of other destructive processes to which the material was exposed during processing.

Processes of pyrolysis and burning of PVC were investigated in detail. For example, about 170 substances have been previously identified at PVC thermodestruction within the temperature range below 500°C.⁴ However, all these data can be related rather to a stage of PVC waste products recycling by pyrolysis or combustion. The PVC manufacture stage drew less attention.

Migration of the following substances from a PVC profile observed as a result of our experiments carried out in the manner described in Degradation Procedure section is presented in Table II.

Dibutylphthalate probably had been a part of some lubricant oils on the equipment, therefore it was found on the surface of a product. Presence of aromatic and polycyclic aromatic substances in the emission confirms the existence of cyclization reactions of the degraded polymeric PVC chain under temperature influence of the forming equipment.

From the PVC profile surface, where the surface layer was removed, only emission of naphthalene ($1.67 \mu\text{g}/\text{m}^2$) was determined at 100°C.

Content in hydrogen chloride removed from the surface of researched PVC profiles was also investigated. The total of hydrogen chloride emitted at 100°C comprised $0.6 \text{ mg}/\text{m}^2$ for PVC profile with the removal of surface layer. For a PVC sample without removal of the top layer, the issue of hydrogen chloride at 100°C has comprised $2.1 \text{ mg}/\text{m}^2$. The formation of hydrogen chloride was not revealed from the PVC sample maintained at 50°C.

Another experiment was carried out to examine the possibility of polychlorinated hydrocarbons formation during the analysis in chromatograph. The mixture of hydrocarbons in ethanol, modeling the structure of PVC thermooxidizing destruction products, was prepared. Seven substances were included in the mixture: benzene, toluene, carbon tetrachloride, dichloroethane, methylene chloride, chloroform, and hydrochloric acid. Concentration of each substance in ethanol comprised 5% mass. The mode of chromatography corresponded to one of the mass-spectrometry analyses, but the flame ionization detector with resolution 10^{-12} g on hexane was used instead of mass detector. As a result of the analysis formation, five new chlorine-containing substances were detected. Their total amount was 0.2% sample weight put in chromatograph. Hexachlorobenzene has been used as an internal standard for defining concentration of the newly formed substances. But the experiment revealed no correlation with the structure of the substances emitted from PVC. Thus, it is possible to assert that the results of the analysis of products emitted at PVC thermooxidizing destruction are reliable.

TABLE I
Activation Energy of the Top and Deep Layer of PVC Products

Mark of polymer	Sample of top layer (kJ/mol)	Sample of deep layer (kJ/mol)
Window profile (Rehau)	140	184
Siding (Rehau)	136	186
Siding (Becker-system)	141	182
Window profile (Becker-system)	142	178

TABLE II
Emission from PVC Sample Surface

Temperature at 100°C		Temperature at 50°C	
Substance	Amount, $\mu\text{g}/\text{m}^2$	Substance	Amount ($\mu\text{g}/\text{m}^2$)
Naphthalene	7.00	Naphthalene	3.67
Acetophenone	10.67	2-methyl naphthalene	7.33
Cis 1-cyclohexylmethyl 2methyl cyclohexane	413.29	Cis 1-cyclohexylmethyl 2 methyl cyclohexane	299.64
Anthracene	7.33	Anthracene	6.0
Dibutylphtalate	99.91	Dibutylphtalate	36.66
9-methylanthracene	4.00	–	–
Acetylchloride	32.01	–	–
Biphenyl	74.99	–	–
Chloroform	106.66	–	–
1,1,1-trichloroacetone	3.67	–	–
2,2,2-trichloroethanol	89.99	–	–
1,1,2,3,4,4-hexachloro 1,3-butadiene	23.33	–	–
1,1,2,3,3,3-hexachloro 1-propene	5.33	–	–
Hexachlorobenzene	67.66	–	–
Hexachloroethane	68.99	–	–
Chloromethyl dichloromethyl ester	3.33	–	–
α -oxomethyl ester of benzenacetic acid	33.00	–	–

It is obvious that the substances, which resulted from polymer thermal destruction caused by the heated up metal parts of extrusion equipment are contained in the structure of surface layer. The majority of volatile thermodestruction products evaporated from the material during its processing, whereas some parts of semivolatile and nonvolatile substances were withheld by polymer matrix.

The fact that causes interest is that, practically, all chlorine-containing substances found are chlorinated with the maximum quantity of chlorine atoms and with the preservation of nonsaturated bonds. The given chlorine-containing hydrocarbons cannot be formed with the participation of hydrogen chloride. This fact makes obvious the occurrence of free chlorine radicals in PVC at fusion temperatures.

To establish the reason for the occurrence of chlorinated substances in PVC, we shall consider the available scientific data concerning the formation of polychlorinated substances during various kinds of PVC thermodestruction. The noticeable difference in composition of chlorinated hydrocarbons formed at burning and pyrolysis is that in the presence of oxygen greater amount of chlorine-containing hydrocarbons with double bonds (dichlorobutadiene, dichlorobenzene, and trichlorobenzene) appear. Some nonsaturated chlorine-containing hydrocarbons formed at burning (dichlorobutylene, trichlorobutylene, dichloropentadiene, and dichlorocyclopentene) generally do not appear in composition of gas phase at PVC pyrolysis.⁷ Proceedings from these data, it is logical to assume that most likely PVC destruction at extrusion occurs with the participation of oxygen. It is obvious that the mechanism of destruction is radical because the processing temperature usually does not exceed 200–

220°C. Preservation of double bonds in found chlorinated hydrocarbons allows to assume that their formation occurs by means of a substitution reaction. It is possible that with the participation of oxygen various oxygen-containing compounds are formed. They serve as the initiation of radical reactions by which the chlorine radical participating in substitution reactions is formed. The formation of polychlorinated compounds is typical for PVC thermodestruction at low temperatures. The conducted research marks that by the rise of burning temperature the formation of polychlorinated hydrocarbons is slowed down and their decomposition starts to prevail.⁸

It is possible to judge indirectly about the possibility of polychlorinated substances formation during PVC processing by the structure of polychlorinated dibenzodioxines and polychlorinated dibenzofuranes found in blood tests of workers at PVC processing and manufacture enterprises. In workers' blood tests, the increased levels of 1,2,3,4,6,7,8-hexachloro and 1,2,3,6,7,8-heptachlorodibenzofuranes⁹ were found. This confirms the data about the possibility of almost a maximum polychlorinated substances present in the surface layer of the PVC.

It is known that iron and its salts, for example, chlorides as Lewis's acids can well catalyze reactions of chlorination by means of substitution.¹⁰ For example, the research marked that the quantity of polychlorinated hydrocarbons, in particular, dibenzodioxines and dibenzofuranes, repeatedly increased at addition in burning zone of metals chlorides, which worked as catalysts for chlorination reactions.¹¹ Undoubtedly, metal details of extruder in the manufacture of PVC products contain some chlorides, owing to the emission of hydrogen chloride from PVC at processing. The

surface PVC layer contacts the walls of extruder, and iron chlorides acting as catalysts of substitution reaction result in higher degree of PVC destruction and appearance of polychlorinated substances on the product's surface. It is possible to explain the appearance of polychlorinated substances on PVC surface by the catalytic ability of iron chlorides. The polychlorinated substances cannot be formed without catalytic effect of salts inside PVC layers, which are heated up approximately to the same temperature as the surface. PVC thermodestruction occurs inside polymer material as well. Hydrogen chloride and polycyclic aromatic substances found both in external and internal layers of PVC profile testify to it. But chlorinated hydrocarbons are found only in the external surface layer. It confirms the assumption that metal of the equipment and, in particular, its salts in contact with material caused greater degree of polymer destruction, because during polymer processing in extruder the gradient of temperatures in polymer is not great enough to cause large difference in PVC destruction products in surface and internal layers.

Considering the facts obtained from this investigation, it is possible to assume that a certain share in PVC destruction during its processing is brought about by metal of extruder, forming machine, etc. It is possible that by drawing the heat-resistant layer of ceramic, polymer, or other protective coating on internal parts of forming machines it will become possible to reduce PVC destruction during processing, and it will allow to increase the processing temperatures, productivity of the equipment, reducing emissions in the air of a working zone, and to make the material cleaner at the using stage.

Emission of potentially harmful substances from PVC surface do not exceed the established norms, although existing norms are designed for the emissions from a mass unit, instead of the one received from a surface. The attempt taken to recalculate the superficial emission determined during the experiment, into mass emission (the weight of samples was known), it was discovered that it was several times less than the allowable norms. It is possible to mention final emission from the PVC surface, because the emission does not exist in a deep sample cut as the results of experiment have demonstrated. In the article,¹² the author states that at use of PVC products in water the emission of some harmful substances take place during some initial days of usage and it creates the concentrations,

which exceed maximum permissible concentration. However, in some days, the emission stops. This once again confirms the existence of emission from a surface of absolutely new PVC product at the initial stage of its use. Thus, the majority of substances determined on polymer surface are not volatile and possess low toxicity, with some exception, and during the use under common conditions they represent no danger and can be eliminated from surface by washing.

However, the phenomenon of superficial emission from PVC polymer surface takes place and it is necessary to pay attention to some substances, which remain in a polymeric matrix.

CONCLUSIONS

Results obtained from this work suggest the influence of metallic element from the equipment affecting the polymer destruction process during extrusion. It concentrates degradation products in the surface layer of PVC. Results of researches are applicable for sanitary-and-hygienic estimation of PVC products, PVC emission in the air at extrusion of PVC products, and also for the development of new effective methods of stabilization of the given polymer during processing aimed at suppression of chlorine radical content in polymer and blocking of catalytic metal chlorides action.

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