

Characterization of PVC Cable Insulation Materials and Products Obtained after Removal of Additives

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ABSTRACT: Organic solvents cyclohexane, dichloromethane, hexane, and tetrahydrofuran were tested to separate the dioctylphthalate (DOP) as plasticizer from the poly(vinyl chloride) (PVC)-based materials. It was found that the efficiency of ultrasound-enhanced hexane extraction of the DOP from PVC is 70% and the efficiency of the separation of the DOP and other compounds from the PVC by dissolution in THF followed by subsequent precipitation was 98–99%. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were used to characterize the thermal behavior of PVC materials before and after extraction of plasticizers. It was found that during heating in the range 20–800°C the total mass loss measured for the nontreated, extracted, and precipitated PVC samples was 71.6, 66.6, and 97%, respectively. In the temperature range 200–340°C, the release of DOP, HCl, and CO₂ was observed by simultaneous thermogravimetry (TG)/FTIR. The effect of plasticizers on thermal behavior of PVC-based insulation material

was characterized by DSC in the range –40–140°C. It was found that, concerning the PVC cable insulation material before treatment, the value of the glass transition temperature (T_g) was 1.4°C, whereas for the PVC sample extracted by hexane, the value of T_g was 39.5°C and for the PVC dissolved in THF and subsequently precipitated, the value of T_g was 80.4°C. Moreover, the PVC samples after extraction of plasticizers, fillers, and other agents were tested to characterize their thermal degradation. The TG and FTIR results of chemically nontreated, extracted, and precipitated samples were compared. The release of DOP, HCl, CO₂, and benzene was studied during thermal degradation of the samples by FTIR. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 788–795, 2006

Key words: PVC; thermal degradation; thermogravimetry/FTIR; differential scanning calorimetry; plasticizer extraction

INTRODUCTION

In recent years, the recycling of poly(vinyl chloride) (PVC) materials became an actual task.^{1–3} The technological approaches are based on the PVC treatment with organic solvents [such as methyl ethyl ketone or tetrahydrofuran (THF) and other solvents^{1,4–7}] to extract compounds serving as plasticizers, antioxidants, flame retardants, etc., and to achieve partial or total dissolution of the PVC matrix. The PVC solution is treated by azotropic distillation, centrifugation, or

filtration, and the dissolved PVC can be precipitated by addition of other suitable agents (e.g., water, methanol) in which PVC is not soluble. This approach has been considered as economically sound and environmentally friendly² and suitable for the recycling of PVC materials. Detailed information about chemical and thermal degradation of PVC-based materials is necessary in the assessment of eco-toxicological risk during accidental burning and/or recycling of building materials, cables, and other postconsumer products.

In this study, we investigated the extraction of plasticizers from PVC cable insulation materials. Most of the plasticizers are high-boiling organic liquids and their function is to reduce the glass transition point (T_g) of the plastics to a level below the temperature used in the actual application of the plastics. Their effect is to decrease the brittleness of the plastics and to increase the service life of PVC materials subjected to elevated temperatures for long periods of time.⁸

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Phthalate esters are the most commonly used plasticizers [e.g., dioctylphthalate (DOP), diisooctylphthalate (DIOP), diisononylphthalate (DINP)].

To find optimal conditions for recycling commercial PVC cable insulation material, the extraction efficiency of organic solvents, such as cyclohexane, dichloromethane, hexane, and tetrahydrofuran, were tested for the separation of a plasticizer. In this study, two methods were used for the PVC chemical treatment, namely, ultrasound-enhanced hexane extraction and the dissolution in THF followed by the subsequent precipitation of PVC. Methods of thermogravimetry (TG)/FTIR were used to elucidate chemical processes that caused the PVC thermal degradation on heating in air and to compare thermal behavior of the PVC samples before and after separation of plasticizer.

In our previous study,⁹ the chemically nontreated commercial PVC cable insulation material was investigated on heating in air and nitrogen. No substantial differences were observed by TG in the thermal degradation of PVC samples when heated in air or nitrogen the temperature range 200–340°C.

EXPERIMENTAL

Gas chromatography

Gas chromatography GC-MS (Agilent 6890 Series GC System with Agilent 5973 Mass Selective Detector) was applied for the analyses and the direct chemical identification and quantification of the organic compounds were used as plasticizer for PVC.

GC column produced by J&W Scientific (30 m × 250 μm × 0.25 μm DB 5) was used. Temperature program was as follows: start temperature, 55°C, 10 K/min from 55 to 250°C, 1 min at 250°C, 10 K/min from 250 to 290°C, 15 min at 290°C; carrier gas: He, 1.4 mL/min; column head pressure, 1.24 bar; inlet: splitless, 290°C; injection volume, 1 μL; MS detector: source, 230°C, quadruple, 150°C.

Phthalate standards (Fluka, Munich, Germany) dissolved in dichloromethane were analyzed by GC under the same conditions as the real samples. Identification of phthalates was performed by comparing the retention time (t_R) of GC peaks of the samples with the t_R of phthalate standards. Moreover, the respective MS spectra of the compounds determined in the GC peaks were compared with NIST MS library data.¹⁰

TG-FTIR spectrometry

TG/FTIR apparatus-TG 209 system (Netzsch Ltd., Selb, Germany) coupled with a vector 22 FTIR Spectrometer (Bruker Optics, Ettlingen, Germany) was used under following conditions: sample amount, 25 mg; heating rate, 5 K/min; airflow rate, 35 mL/min.

Differential scanning calorimetry (DSC)

The DSC experiments were performed by a TA Instruments Q100 system. The measurements were carried out in nitrogen in the dynamic mode at the heating rate of 15 K/min in the temperature range from -40 to +130°C. To obliterate the effect of thermal history on the T_g temperature determination, the DSC measurements were carried out subsequently during heating, cooling, and reheating runs. The reheating run was used for determination of glass transition temperature (T_g). Aluminum crucibles were used, and the sample amount was 10 mg.

Samples

Commercial PVC cable insulation sample from Varia Prague Co. (Prague, Czech Republic) was used as starting material in this study. It contained the following additives: DOP in the amount of 22% w/w as plasticizer, chalk as filler, thermal stabilizer (Pb-based compound), lubricants (Pb and Ca stearate), and carbon black as a photostabilizer.

The extracted sample was prepared by ultrasound-enhanced hexane extraction and the precipitated sample was prepared by dissolution in THF and the subsequent precipitation of PVC. Two methods were used for the separation of plasticizers, fillers, and other agents from PVC samples.

Methods used for chemical treatment of PVC samples

Ultrasound-enhanced hexane extraction

One gram of grated PVC sample was shaken with a known volume of hexane under ultrasound treatment for 30 min (the ratio of PVC mass to hexane volume varied from 3 to 70 mg/mL). After filtration, the hexane solution of plasticizer was used for gas chromatography coupled with mass spectrometry (GC-MS) analysis. The solid PVC was considered extracted.

Dissolution by THF

One gram of grated PVC sample was transferred to a glass bottle with a known volume of THF (the ratio of PVC mass to THF volume was 10 mg/mL). The ultrasound treatment was used until the solid sample was completely dissolved (~5 min). The use of this method enabled us to dissolve totally the PVC cable insulation sample. The turbid solution was filtrated through glass fiber paper (Schleicher & Schnell, Germany), and the clear solution was concentrated by using rotary evaporator. The PVC dissolved in THF was precipitated by methanol. Precipitated solid PVC was separated from the remaining solution by filtration. The solid PVC was denoted as precipitated.

Soxhlet extraction in either dichloromethane or cyclohexane

One gram of grated PVC sample was extracted with 75 mL of the respective solvent for 1 h at 60°C. The solution was concentrated by using a rotary evaporator. This remaining solid PVC sample was not further characterized in this study.

RESULTS AND DISCUSSION

Extraction of organic additives from commercial PVC cable insulation

The following organic solvents, cyclohexane, dichloromethane, hexane, and THF, were used in this study for the extraction of plasticizers and other additives. The content of plasticizers (phthalates) in the solvents after extraction was determined by GC-MS technique and by an external standard method using the calibration curve¹¹ of DOP.

It was found that the organic solvents used exhibited different efficiency for extraction of DOP. The efficiency of cyclohexane was very low; the efficiency of dichloromethane was higher, but PVC was partially dissolved in dichloromethane and could be precipitated by the addition of water or methanol. By using hexane in the ultrasound-enhanced extraction, the partial extraction of DOP took place, but no PVC was dissolved during extraction. A duration of 30 min was used for the hexane extraction to get a sufficient amount of the DOP for its chemical determination.

To test the conditions for the DOP extraction, different ratios of PVC solid to hexane solvent volume were used. From the results presented in Figure 1, it followed that 70% extraction efficiency was achieved

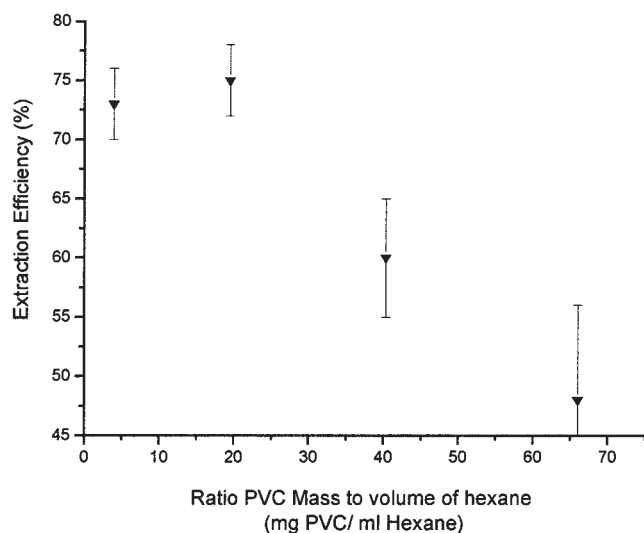


Figure 1 Diethylphthalate (DOP) extraction efficiency by hexane from PVC cable insulation as dependent on the ratio of solid PVC/volume of hexane solvent.

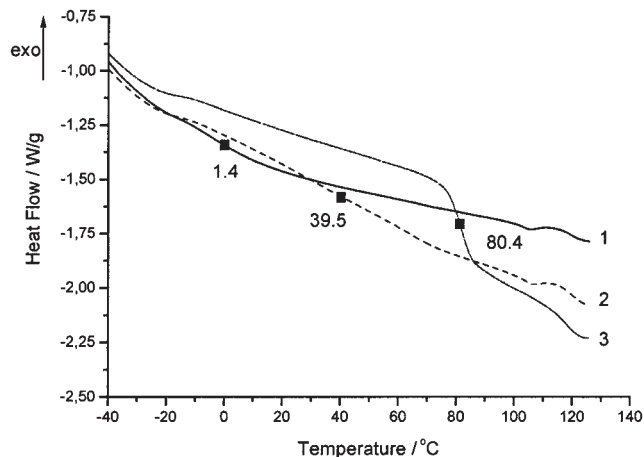


Figure 2 DSC results characterizing of thermal behavior of PVC samples: curve 1, chemically nontreated; curve 2, extracted; curve 3, precipitated. Heating in nitrogen at the rate of 15 K/min.

for the ratio lower than or equal to 20 mg PVC/mL of solvent. The extraction efficiency decreased considerably when a higher amount of PVC was used for the same amount of the solvent. The separation of DOP and other compounds was achieved by total dissolution of PVC by using THF. Methanol was used for the subsequent precipitation of PVC from the THF solution. The precipitated solid PVC was separated from the solution by filtration and the amount of DOP was determined in the remaining solution; the extraction efficiency by THF was 98–99%.

Thermal characterization of PVC cable insulation samples before and after chemical treatment: Influence of the amount of plasticizer in PVC on its glass transition temperature (T_g)

A plasticizer behaves similar to a solvent when mixed into a polymer and results in the lowering of the T_g and by this way influences its flexibility. To compare the effect of the extraction on the sample thermal behavior, the values of T_g were determined for chemically nontreated, extracted, and precipitated samples by DSC. The DSC results plotted in Figure 2 show that the T_g values decreased with the increasing content of plasticizer: for the chemically nontreated sample, that contained 22 wt % DOP as plasticizer, the T_g value was 1.4°C (curve 1 in Fig. 2). For the extracted PVC sample (where the 7 wt % DOP remained after extraction), the T_g value was 39.5°C (curve 2, Fig. 2), and for the precipitated sample (where 0 wt % of DOP was present), the T_g value was 80.4°C (curve 3, Fig. 2). These results are in good agreement with the literature data.^{12,13}

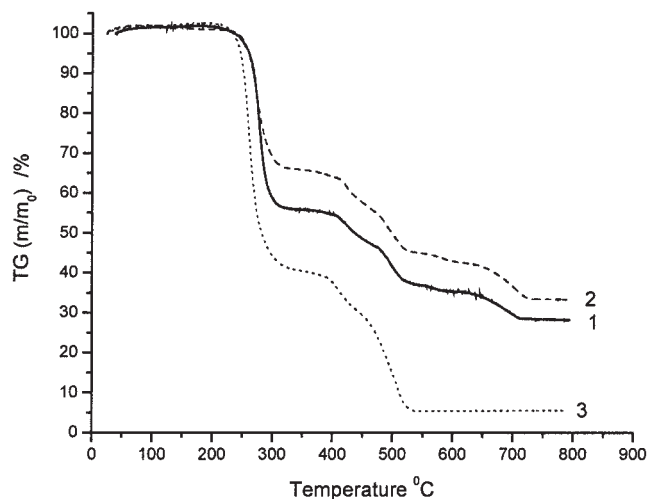


Figure 3 Results of TG obtained during air heating of PVC samples: curve 1, chemically nontreated; curve 2, extracted; curve 3, precipitated.

Thermal stability of the PVC samples and processes taking place during thermooxidative degradation

To understand the processes taking place on air heating of the PVC samples before and after chemical treatment, the TG/FTIR measurements were carried out. Figure 3 depicts the TG curves of the PVC samples in the range 20–800°C. Curve 1 corresponds to the chemically nontreated sample; curves 2 and 3 correspond to the extracted and precipitated samples, respectively.

The mass loss values determined (Table I) by TG for chemically nontreated sample are as follows: 45.9% in the range 200–340°C; 17.2% in the range 360–540°C; and 8.5% in the range 540–800°C. From FTIR spectra [Fig. 4(A)] it followed that in the range 200–340°C the release of phthalate, HCl, and CO₂ took place. We assumed that the CO₂ release occurred as the result of the reaction between HCl and CaCO₃ (chalk) that was present as filler in the PVC sample. The release of CO₂ observed around 400°C was due to the intense burning of the polymer backbone, while the release of CO₂ on heating from 500 to 800°C was due to the thermal degradation of the carbonate fillers. The mass spectrometry results presented in our previous study⁸ con-

firmed the findings of this study, namely, that the heating of PVC sample in the range 200–340°C was accompanied by the evolution of HCl ($m/z = 36$; m/z is the mass to charge quotient corresponding to H³⁵Cl fragment determined by mass spectrometry) that took place because of dehydrochlorination of PVC. Moreover, it was found in our previous study⁸ that, besides HCl, the release of benzene ($m/z = 78$) and di-*n*-octyl phthalate DOP ($m/z = 149$) was observed in the temperature range of 200–340°C. Our results are in agreement with the finding published by Matuschek et al.,³ who reported the release of phthalate-based plasticizer ($m/z = 149$) along with the release of HCl ($m/z = 36$) from the PVC sample in the range 320–420°C. Therefore, we assumed that the PVC backbone degradation took place partially in the range 200–340°C along with the dehydrochlorination and evaporation of some additives.

From TG results of the extracted sample (Fig. 3, curve 2), it followed that the second and third degradation step of the PVC cable insulation took place in the temperature intervals 360–530 and 530–770°C, respectively.

The mass loss values of the extracted sample are summarized in Table I: 35.3% in the range 200–340°C, 19.7% in the range 360–540°C, and 11.6% in the range 540–800°C. FTIR spectra [Fig. 4(B)] confirmed that the lower amount of phthalate was released during heating of extracted sample as compared to the chemically nontreated sample [Fig. 4(A)]. Moreover, in the range 200–340°C, a part of the released HCl reacted with the carbonate forming CO₂ [Fig. 4(B)] similarly to the nontreated sample. From Figure 4(A) it followed that the CO₂ release due to degradation of the polymer backbone of the extracted sample took place at about 400°C and that, again, the decomposition of the carbonate-based fillers occurred in the range 540–800°C, similarly to the nontreated sample [Fig. 4(A)].

From TG results of the precipitated sample (see Fig. 3, curve 3 and Table I), it followed that the thermal degradation took place in the range 200–340°C (62.3%) and in the range 360–550°C (34.7%). The relatively high mass loss (97%) of this sample can be explained that during the dissolution/precipitation process the organic additives (plasticizers, etc.) and inorganic car-

TABLE I
Values of the Mass Loss (wt %) for PVC Cable Insulation Samples on Heating in Air in the range 20–800°C Measured by Thermogravimetry

PVC sample	1. Degradation step (200–340°C)	2. Degradation step (360–530°C)	3. Degradation step (530–800°C)	Total (20–800°C)
Nontreated	45.9%	17.2%	8.5%	71.6%
Extracted	35.3%	19.7%	11.6%	66.6%
Precipitated	62.3%	34.7%	—	97%

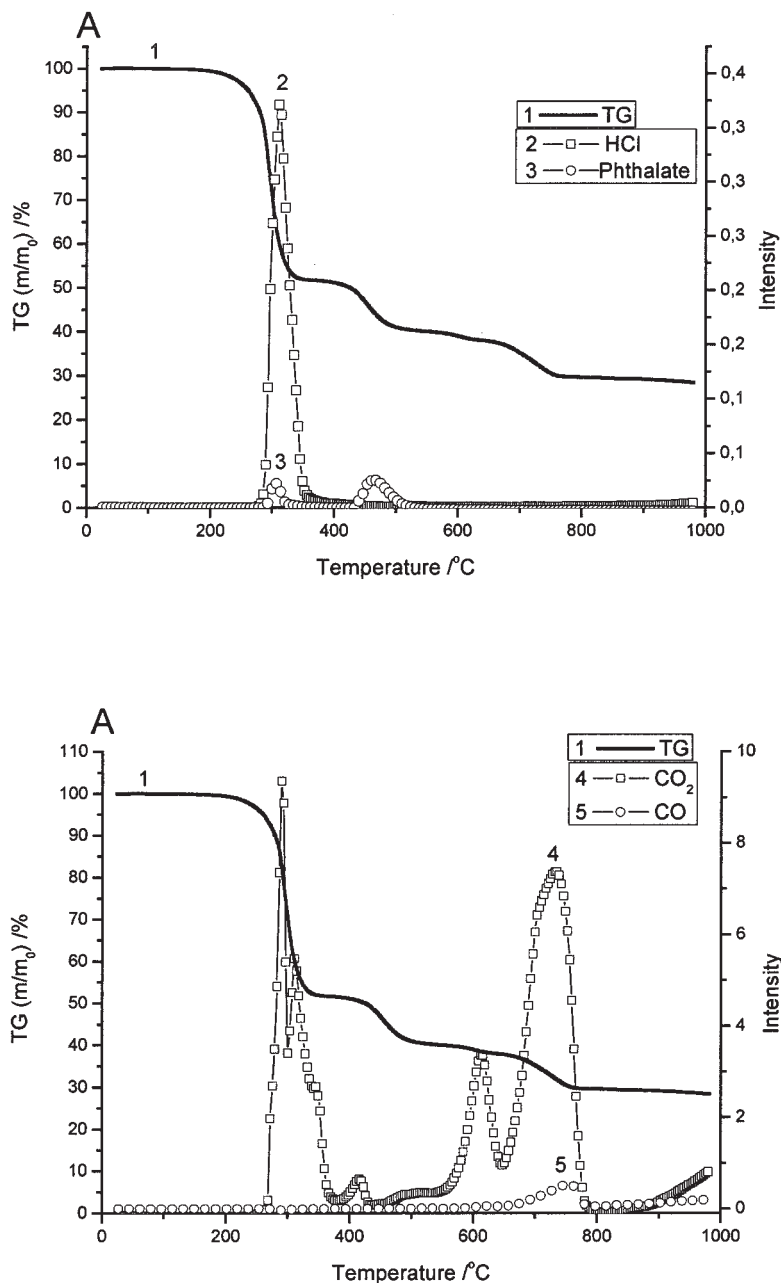


Figure 4 Results of TG/FTIR demonstrating the release volatile products (phthalates, CO, CO₂, HCl) during air heating of PVC samples: A, chemically nontreated; B, extracted; C, precipitated. Curve 1 corresponds to TG results, curve 2 to FTIR spectrum of HCl, curve 3 to FTIR spectrum of phthalate, curve 4 to FTIR spectrum of CO₂, and curve 5 to CO.

bonate-based filler were totally removed. Consequently, it is not possible to directly compare these values.

No release of phthalate was observed on FTIR spectra in Figure 4(C) on heating of the precipitated sample confirming that all plasticizer actually was removed. The HCl release was observed in temperature range 200–340°C, in agreement with the respective TG results in Figure 4(C). The maximal rate of the thermal degradation of the precipitated samples was shifted to

lower temperature by 15 K in comparison with the chemically nontreated or extracted samples (Fig. 3). On heating above 400°C, the release of CO₂ was observed and confirmed the total burning/degradation of the residual polymer backbone. In agreement with our expectations, no release of CO₂ was observed on heating above 600°C with the precipitated sample that was free of carbonate-based fillers. The TG/FTIR results [see Fig. 4(C)] are in agreement with the results obtained by means of TG/DTA/mass spectroscopy on

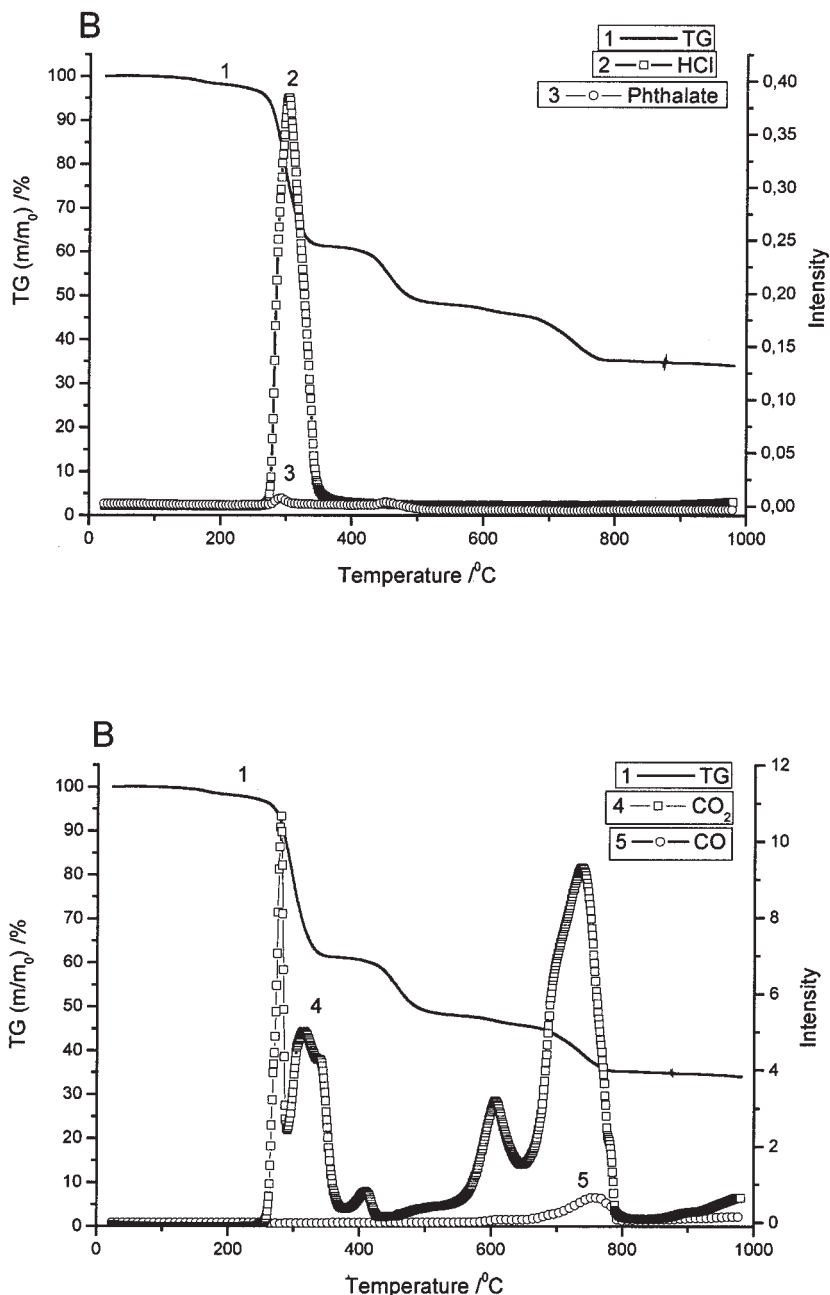


Figure 4 (Continued from the previous page)

heating in air.⁹ The release of HCl was observed in the range 270–330°C and CO₂ release was observed in the range 450–570°C [see ref. ⁹, Figure 2].

CONCLUSIONS

The extraction of PVC cable insulation material by hexane is a suitable way for separation of the plasticizer (DOP) from the sample without dissolution of the PVC matrix. The efficiency of the DOP extraction was 70% by using just 30-min duration of the extraction. The ultrasound-enhanced hexane extraction

method can be recommended for the rapid isolation and identification of the plasticizer. The method of dissolution in THF and subsequent PVC precipitation is suitable for the separation of individual components as admixtures from the plastics.

It was demonstrated by DSC that the DOP amount was totally removed with the chemical treatment used. Moreover, the DSC confirmed the previous statement that the T_g of PVC samples decreased as the content of plasticizer increased. The T_g values ranged from $T_g = 80.4^\circ\text{C}$ for the precipitated sample (where no DOP plasticizer was present) to $T_g = 1.4^\circ\text{C}$ for the

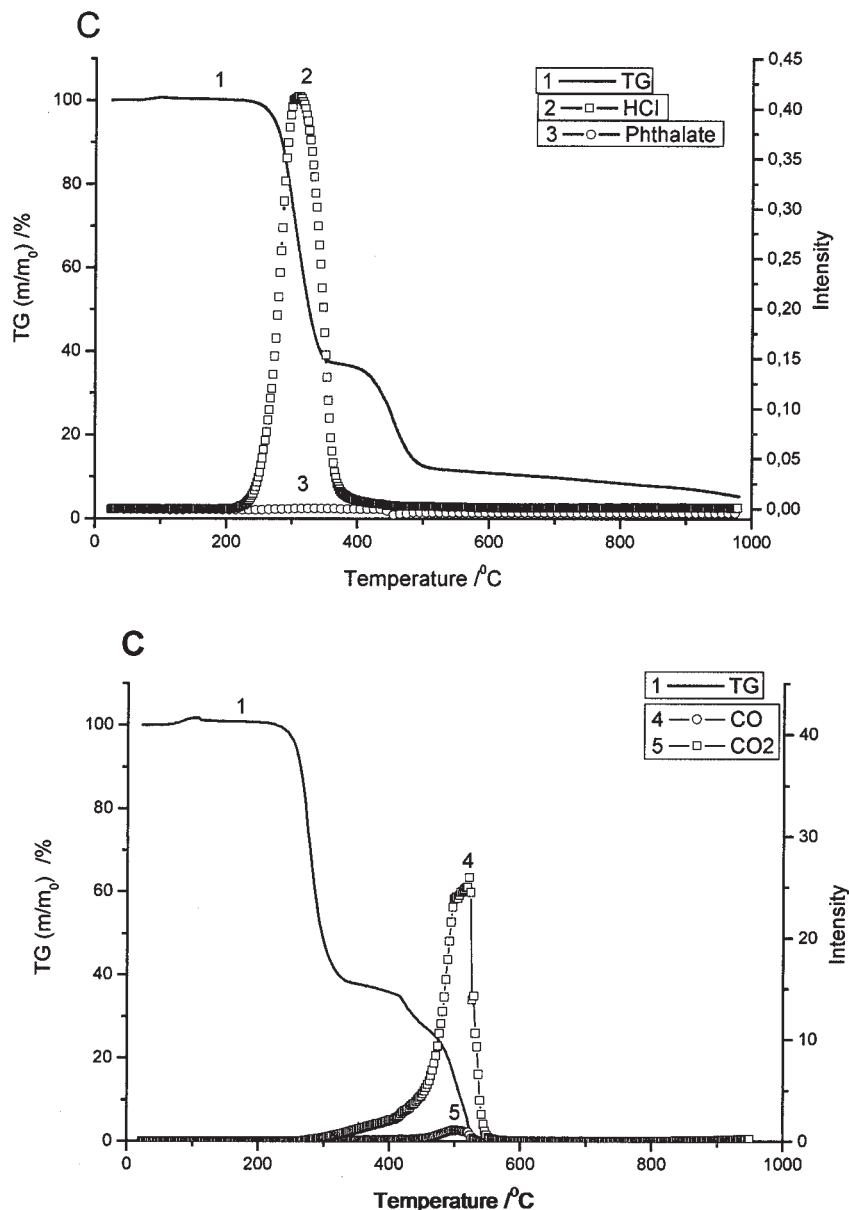


Figure 4 (Continued from the previous page)

chemically nontreated sample (where DOP content was 22%).

Thermogravimetry and FTIR methods were used to elucidate chemical processes that caused its thermal degradation in the range 200–800°C. The total mass loss measured for the nontreated, extracted, and precipitated PVC samples was 71.6, 66.6, and 97%, respectively. It was observed that the precipitated PVC without DOP burned almost completely, whereas 7 and 22% of DOP-containing samples burned about to the 67 and 72% extent, respectively. Hence, decreasing the DOP amount by 70% resulted in the decrease of burning by 5%, which is in agreement with the total mass reduction by about 4% of the sample mass. It must be mentioned, however,

that precipitated sample contained practically pure PVC, whereas the nontreated and extracted PVC sample contained additives. In the temperature range 200–340°C, the release of DOP, HCl, and CO₂ was observed by simultaneous TG/FTIR. The resulting volatile products analysis can be used for environmental risk assessment of the PVC materials burning in cases of fire accidents.

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