

A Recycling Assessment of PVC Bottles by Means of Heat Impact Evaluation on Its Reprocessing

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ABSTRACT: Poly(vinyl chloride) (PVC) products are very convenient for reclaiming and recycling. Therefore, the heat impact at 160–180°C temperature during the recycling process was investigated in the current study by means of spectroscopic studies, such as infrared and ultraviolet, and of differential scanning calorimetry curves. The bottle samples are slightly and considerably affected at 160 and 180°C heat treatments, respectively, which were determined as the formed decomposition products, color change, loss of volatile components, and peroxide formation in air. However, since this decomposition occurred at 30 min of experimental time, which is about sixfold that of real process times, the reclaimed material found recyclable as is. Judicious recombination of the powdered reclaimed material making up the lost or consumed component makes possible the use of this material in the production of window sections, profiles, pipes, and even bottles. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 865–869, 1998

Key words: poly(vinyl chloride) (PVC) recycling; packaging materials; PVC degradation; recycling assessment; heat impact on PVC

INTRODUCTION

Research on reclaiming and recycling of plastics has increased in recent years as the environmental consciousness has increased. Poly(vinyl chloride) (PVC) today is one of the most used thermoplastics. Much of the disposable medical devices are made of PVC.¹ In the United States, 9% of municipal solid waste is comprised of plastics and about 39% of it is comprised of packaging materials.² In Europe, about 18% of all PVC is consumed in the form of packaging.³ PVC packaging materials are mainly used in food, cleansing materials, textile, and blood packing in the form of bottle, box, film, clam-shell, and blister. Attacks against PVC are mainly because of the suspect of releases containing harmful chlorine compounds, particu-

larly vinyl chloride and dioxin derivatives, during their production and incineration, and in landfills.^{3–5} Nevertheless, most of the concern about emissions is based on a lack of information.¹ The contribution of PVC to harmful releases in the environment is not to such a great extent, particularly after the recent developments yielding environmentally conscious products.³ In addition, the Chlorine Chemistry Council continues its works for the investigation, precaution, and legislation from environmental aspects.^{5,6}

Although the harmful effects of aforementioned released agents, plasticizers,⁷ and some heavy metal additives³ have been alleviated, landfilling is still a problem because of space. Hence, reclamation and recycling of PVC gains importance to decrease the municipal load and the released species in the landfills to a certain extent.

Bottle-to-bottle recycling of PVC began in the late 1980s.⁸ There was no infrastructure for its collection and recycling until a few years ago. Today, however, recycling products constitute a lu-

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crative market with convenient know-how, sufficient equipment, and instrumentation.^{9,10} Recycled PVC bottles contain tin, zinc, and calcium stabilizers, and they give marketable, quality profiles.¹¹ These type of materials are evaluated in the production of window frames, profiles, pipes, and although more restricted, of bottles.⁹ PVC bottle scraps are particularly suitable for rigid foam profile production since they are made up of the same molecular weight PVC. The coextrusion process allows for manufacturing layered products, which comprise both raw and recycled material in different layers.¹¹ Recycling also saves energy and the raw material cost, besides having environmental benefits.¹²

Research on reclaiming and recycling of plastics, of PVC, in particular, is increasing and focusing on the following topics^{1,2,8-13}:

1. Development of techniques, methods, and instrumentation for sorting of PVC;^{8-10,14-16}
2. Modification and process studies to provide compatibility of PVC with other plastics;¹⁷⁻¹⁹ and
3. Survey on new application areas and related modification or technique investigations for the use of recycled PVC.^{1,8,9,20,21}

The study presented herein has been carried out for the possible assessment of recycling of the reclaimed post-consumer PVC bottles used for water and mineral water. Thereby, the impact of certain heat treatments, which are likely to be applied in the course of their reproduction process has been examined on the strips cut out of PVC bottles.

EXPERIMENTAL

The samples cut out of blue-colored PVC bottles in the market were taken into an air-circulating oven at 160, 180, and 220°C for 30 min. DSC curves of the samples before and after the heat treatment were taken by using a Setaram DSC 92 instrument, in aluminium pan. Heating from 25 to 220°C at 10°C/min rate and then cooling with air was applied.

A weight loss experiment was also performed to find out the amount of lost substance during reprocessing. A weighed small strip of PVC was heated at 180°C for 30 minutes in the oven, and it was weighed again.

An ultraviolet (UV) analysis by using a Jasco

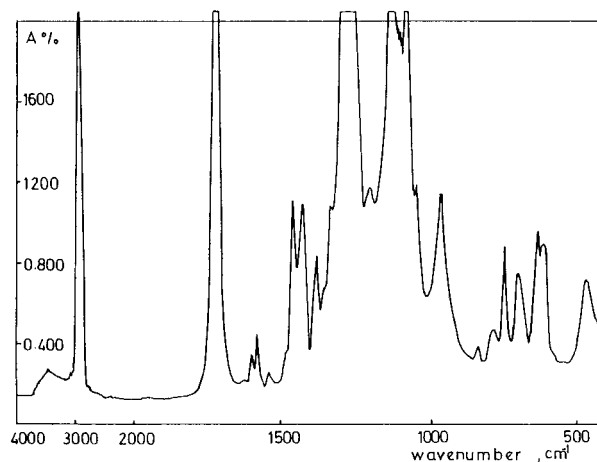


Figure 1 IR spectrum of the cast PVC film.

7800 UV-visible (UV-vis) spectrophotometer and infrared (IR) analysis by using a Shimadzu IR-470 spectrophotometer were applied at room temperature to the strips cut out of the PVC samples before and after the heat treatment. In addition, the IR spectrum of a cast film was also taken. This film was cast from tetrahydrofuran into a petri dish, and its composition (as weight) is PVC powder (Petkim, P38/74), 100 parts; zinc and calcium stearates (Merck), 0.275 and 2.750 parts, respectively; epoxidized soy bean oil (Akdeniz Kimya, Akstab, Alpex 5.6), 5.0 parts; and dioctyl phthalate (DOP, Sankim), 60 parts.

RESULTS AND DISCUSSION

The IR spectra of the cast film (Fig. 1) and the PVC bottle strip (Fig. 2) before the heating process exhibited the same bands, although their intensities are not the same. Thus, the same species are expected in the bottle sample as in that of cast film. 800–700-cm⁻¹ twin bands, which are attributable to stearate-type stabilizers²² and 1570- and 1530-cm⁻¹ bands, which are attributable to zinc and calcium stabilizers,²³ decreased their intensity to a certain extent after heat treatment. Volka et al.²⁴ observed a similar intensity decrease at 1550 cm⁻¹ on the heating of cadmium stearate containing PVC samples. Thermal decomposition can also be observed on the 1700-cm⁻¹ band, becoming deeper because of the carboxylic acids forming by the evolved hydrogen chloride out of PVC.²⁵ Formation of hydroperoxides under thermal treatment by the air oxygen is observed as the increasing band width at 3400

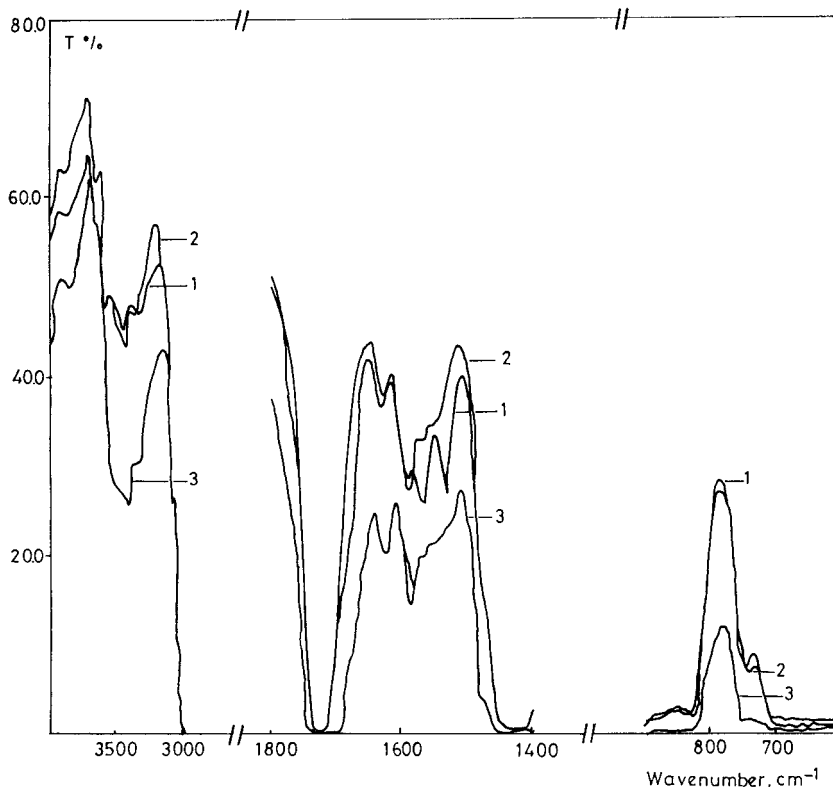


Figure 2 IR spectra of the PVC strips (1) before and (2) and (3) after 160 and 180°C heat treatment, respectively.

cm^{-1} .²⁶ The higher the applied temperature at heat treatment, the higher the amount of carboxylic acids and hydroperoxydes, as implied the band intensities on IR spectra.

Ester bands at 2950 and 1720 cm^{-1} imply that there is a plasticizer like DOP. The plasticizer still exists in the composition after heating for 30 minutes at 160 and 180°C, as understood from the ester bands.

Glass transition temperature (T_g) of unplasticized PVC is about 81°C,²⁷ and it lowers when plasticized. Differential scanning calorimetry (DSC) curves depicted in Figure 3 exhibit a shift of T_g value from 62 to 80°C as the PVC strips heated. Annealing is likely the cause of this T_g shift, which removes the effects of strains caused by yielding and cold drawing. However, a weight loss about 0.3%, observed under similar severe experimental heating conditions, implies the depletion of some ingredients, to a certain extent, acting as plasticizer.²⁸ The cooling section of the DSC curves indicates the same transition of about 80°C.

However, the melting points of zinc and calcium stearates are 130 and 179–180°C, respectively.²⁹ The possibility that some impurities tak-

ing place in the stearates may also decrease their melting point should be taken into account during the evaluation of the heat impact on stearates using the DSC curves. Such an effect and the fact

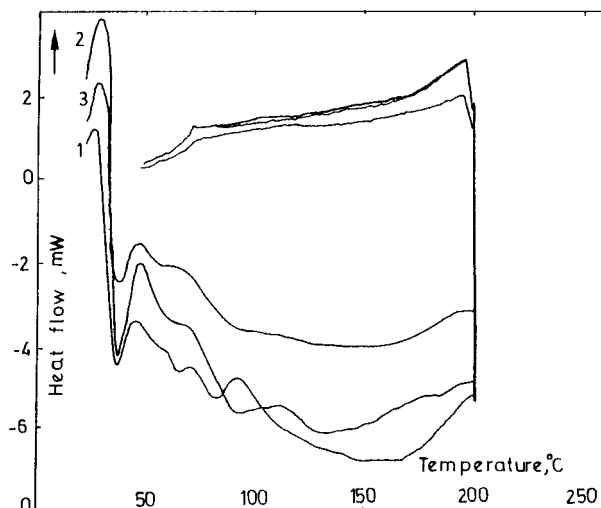


Figure 3 DSC curves of the PVC strips (1) before and (2) and (3) after 160 and 180°C heat treatment, respectively.

that the stearates keep their entity and crystalline structure in PVC formulations after pressing at 160°C for about 16 minutes was observed in a former work.²³ Before and after heat treatment of the current study at 160°C, the stearate melting peak is determined on the DSC curves of strips. However, neither the samples after heat treatment at 180°C on heating region nor any of the samples on cooling region of DSC curves showed such a peak. Braun et al.²⁸ observed that the glass transition temperature of PVC samples with heat stabilizers attained after consecutive annealing up to 200°C at a value of the PVC samples without stabilizer. They attributed this behavior to the consumption of stabilizer in the heating process.

From the point of stabilizer consumption, heating time has to be accounted for, as well as heating temperature, for keeping the product not decomposed in heating process.²⁶ The residence time in the extruder is as short as only a few minutes, and PVC does not exhibit a considerable deterioration in this period.¹⁹ Thirty minutes of heating, which is quite longer than that of real processes, were applied on purpose to make the heating impact much more severe and discernable, thus making the analyses in the laboratory easier. Plastics with zinc-based stabilizers undergo a decomposition, giving colloidal carbon at high temperature, turning the material into black. The strips kept at 220°C to determine the heat resistance threshold scorched and turned into black, as expected. While heat treatment at 180°C turns the strip into yellowish green, only a slight haziness was observed on the strip heated to 160°C.

PVC has no absorbance at 230–450 nm.³⁰ The high absorbance observed on this region (Fig. 4) supports the IR evidence about the existence of plasticizer. The UV spectrum of the strip before heat treatment shows a peak at 236 nm, which is particularly attributable to Dioctyl phthalate (DOP).³¹ After the heat treatment, the UV spectra showed a high absorbance between about 280–420 nm, which is attributable to 4–8 C=C bonds as chromophore groups.³² The forming of these conjugated diens (polyenes) is the evidence of decomposition by releasing hydrogen chloride.^{22,26,32}

Thereafter, once the polyene sequences are formed, these polyenes can absorb UV radiation, which has enough energy to continue decomposition.³³ Thus, the hydrogen chloride that evolved when the PVC degraded is sufficient to catalyze the lengthening of polyene sequences.³⁴ Therefore, it is of great importance the use of judiciously

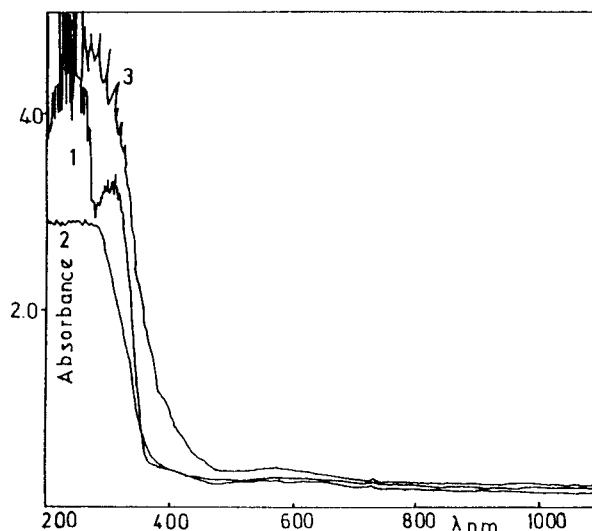


Figure 4 UV spectra of the PVC strips (1) before and (2) and (3) after 160 and 180°C heat treatment, respectively.

chosen stabilizers in the composition of either raw or recycled PVC-based materials.

Ruijian et al.³⁰ achieved diminishment of the amount of polyenes formed at 30 minutes at 180°C from 10 to 3% by using tin-based stabilizers. A stronger stabilizer and compatible synergistic mixtures can be used in PVC formulations convenient for that using area.³³ However, some heavy-metal-containing stabilizers prone to be extracted by rainwater to an unacceptable extent have to be strictly avoided, respecting environmental concerns. Summing up, suitable compositions and processing conditions can give rise to the reproduction of recycled PVC as new products. Thus, the piles of PVC do not occupy space in the landfills, making the present problem remediable.

CONCLUSIONS

Decomposition of PVC strips after severe experimental heat treatments was determined as below.

1. Color change was inspected by bare eyes as a direct evidence of decomposition.
2. UV-vis spectra indicated the existence of certain compounds and the formation of polyene sequences, justifying the bare eye inspection.
3. IR spectra showed special bands attributed to certain compounds either disappearing because of their loss due to volatility or con-

sumption or forming as the decomposition products.

4. DSC curves exhibited a T_g shift to higher values, which is attributable to the loss of components affecting as the plasticizer. It was also confirmed by the weight loss experiment.

Although there are a considerable heat impact at 180°C treatment, and a slight heat impact at 160°C treatment, experimental processes applied herein are quite longer than real ones. Therefore, only negligible heat impact is expected during real processes. Thus, it seems possible to use recycled PVC material for reprocessing with no additive makeup. However, wherever the longer process times are needed, recombination of powdered recycled PVC material with the volatile or consumed components makeup is advisable.

An investigation is planned to perform in the near future with recycled, powdered, and reformulated PVC. The additives must be chosen by considering their reuse area and the environmental concerns. Production of window frames, profiles, and pipes is very convenient for the use of recycled material made up with strong additives. The coextrusion process is convenient for layered products with virgin PVC on the side contacting with the species, which is of importance, and the recycled one on the other side.

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