

Influence of Additional Thermal Stabilizers on the Reprocessing of Postconsumer Poly(vinyl chloride) Bottles

Sevgi Ulutan

Department of Chemical Engineering, Faculty of Engineering, Ege University, 35100 Bornova, Izmir, Turkey

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ABSTRACT: The addition of heat stabilizers is essential for preventing the degradation of poly(vinyl chloride) (PVC) during its processing. The heat stabilizers consumed in the first run have to be made up before the reprocessing of recycled PVC. In this study, solvent-cast films, which were prepared from granulated postconsumer PVC bottles mixed with plasticizers and thermal stabilizers, were used. The films were subjected to various heat treatments. No considerable structural change upon heat treatments at 140–160°C was found in IR and differential scanning calorimetry analyses. Polyene formation observed through ultraviolet analysis was not severe, indicating that the added stabilizers

worked well in preventing degradation. The weight loss during the heat treatments was attributed partly to the decomposition of PVC and the evaporation of volatile components and mainly to the removal of the solvent upon heating. Although this study was conducted with water bottles that were to be recycled, it may be equally well applied to other similarly formulated PVC-based materials, such as packaging films. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3994–3999, 2003

Key words: poly(vinyl chloride) (PVC); recycling; stabilization; thermal properties; plastics

INTRODUCTION

Widespread packaging applications result in large amounts of poly(vinyl chloride) (PVC) for disposal. Disposable medical devices are also mainly produced with PVC.¹ Although poly(ethylene terephthalate) has taken over the place of PVC in bottle applications, PVC is still used for fresh meat and cheese wrapping. Polyethylene is recommended for this purpose, but it is difficult to wrap close to polystyrene trays. The Environmental Act imposes a legal requirement for plastic packaging to be recycled. Plastic bottle recycling has grown rapidly since 1990, but projections suggest that further assistance is required.² The reclamation and recycling of PVC is important for reducing the municipal load and released chemicals in landfills.³

Several studies on modification for recycling and the morphology of recycled polymer blends⁴ and PVC-based formulations⁵ have been undertaken to alleviate environmental problems. Vivier and Xanthos⁴ applied peroxide modifications to postconsumer plastics. They used a blend prepared that they prepared and each plastic separately. Although a 1% peroxide addition promoted PVC degradation despite the thermal stabilizer makeup, this modification im-

proved the mechanical properties of the polymer blend. Sombatsompop and Thongsang⁵ demonstrated that PVC pipe recycling was possible in combination with virgin-grade pipe and bottle compounds. They found that the higher the recycled PVC loading was, the greater the hardness and the density were of the blends. The porosity of their products, as determined by scanning electron microscopy, was concluded to be a result of hydrogen chloride gas that evolved upon PVC decomposition. This porosity, as well as gelation that occurred at a high processing temperature (210°C), led to a high swelling ratio. Wenguang and La Mantia⁶ found that the particle size and restabilization of recycled PVC were the two main points to be considered for obtaining virgin/recycled PVC blends with uniform and good mechanical properties. They also found that the addition of recycled bottles and pipes to pipe-grade PVC resin lowered the thermomechanical properties and improved the impact strength and processing behavior, whereas the modulus and tensile strength did not change considerably. Xu et al.⁷ showed that the milling of PVC led to a decrease in the molecular weight but improved the processability, degree of gelation, and mechanical properties. They observed a decrease in the crystallinity through crystalline absorption bands at 604, 635, and 1427 cm⁻¹ and an increase in amorphous absorption bands at 615 and 1435 cm⁻¹ in their Fourier transform infrared study. They proposed that milled PVC could be used as an innovative processing aid, fulfilling the idea of plasticizing PVC itself.

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Correspondence to: S. Ulutan (ulutans@eng.ege.edu.tr).

In a previous study,³ it was observed that discoloration occurred on PVC bottle strips when they were heat-treated, particularly at high temperatures without a heat-stabilizer makeup. This was attributed to the consumption of heat stabilizers during the production of bottles. Degradation was followed by the formation of new products and the depletion of certain materials with spectrophotometric methods, as well as weight loss. Polyene formation was followed by ultraviolet-visible (UV-vis) spectroscopy. Behnisch and Zimmermann⁸ studied the kinetics and mechanism of polyene formation on PVC. They detected polyene groups with various sequences in the form of separate peaks. Several aspects of polyene formation during PVC degradation were also found by Wypych.⁹

The polyene formation on strips taken out of PVC bottles, when directly subjected to heat treatment,³ suggested that the remaining stabilizers in the material from its initial formulation were not sufficient. Thus, it can be concluded that reformulation with a heat-stabilizer makeup is essential for preventing PVC degradation in recycling processes. The additives exhibiting high performance in their first application will continue their positive effects in recycling. This approach will also remedy the compatibility problems of different additives. Calcium-zinc-based stabilizers, however, exhibit lower efficiency than lead- and tin-based stabilizers but are superior to lead-based stabilizers with respect to toxicity and superior to tin-based stabilizers with respect to cost. Calcium- and zinc-based stabilizers act as lubricants in PVC. Calcium-based stabilizers aid with fusion and increase the viscosity.¹⁰

A good-quality foam profile can be made from PVC bottle recyclate. Thomas and Quirk¹¹ showed that using up to 100% bottle recyclate did not affect the density, cell structure, or impact properties of the coextruded foam profile.

Because the formulations used in plastic products vary with the final product, recycled bottles should be reformulated with the addition of the appropriate stabilizers. The objective of this study was to determine an appropriate thermal stabilizer system for the recycling of postconsumer PVC water bottles. For this purpose, the bottles were ground and reformulated to prevent thermal decomposition during processing due to the loss and consumption of heat stabilizers. The influence of heat treatments applied to solvent-cast films was investigated through the thermal and structural changes and the weight loss.

EXPERIMENTAL

Blue-tinted PVC bottles used for water, which were characterized with thermal and spectroscopic methods in a previous study,³ were used. The samples, about 1 cm² cut out of label-free parts of the bottles,

TABLE I
Weight Loss % of PVC Films during the Heating Process

Temperature (°C)	Time (min)		
	15	30	45
140°C	9.00	10.39	11.66
160°C	12.68	25.63	—

were washed clean and ground with a laboratory-type hammer mill to a diameter of about 1 mm. A hundred parts of this resin material were then reformulated with 0.275 parts zinc stearate and 2.750 parts calcium stearate (Merck, Germany), 5 parts epoxy soy bean oil (EPSO; Akdeniz Kimya, Izmir, Turkey, Akstab, Alpex 5.6), and 20 parts dioctyl phthalate (DOP; Sankim, Gaziantep, Turkey). The mixture was dissolved in methyl ethyl ketone (MEK) at about 80°C in a beaker on a magnetic stirrer, and the PVC/MEK ratio was 1:75 (w/w). Then, the mixture was poured into petri dishes and set aside overnight. The thicknesses of the films stripped off the dishes were about 100–200 μm.

The films were kept in an air-circulating oven set at 140 or 160°C for 15–45 min. Besides the weight-loss measurement, ultraviolet (UV) and IR spectra of each sample before and after the heat treatments were taken. A Jasco 7800 UV-vis spectrophotometer (Japan) and a Shimadzu IR-470 spectrophotometer (Japan) were used at room temperature.

Differential scanning calorimetry (DSC) analyses were performed before and after the heat treatments with a Setaram DSC 92 (France) instrument that heated the samples from 25 to 200°C at 10°C/min in closed aluminum pans.

RESULTS AND DISCUSSION

The working temperature range for PVC is quite limited in real processes. Therefore, the temperature interval applied to this experimental study was also limited. For this plasticized PVC formulation, a temperature interval lower than that in a previous study³ was thought to be more appropriate. The weight loss increased as the heating temperature increased and the heating time increased (Table I). Meanwhile, 160°C treatments for 45 min resulted in severe degradation, which was observed as wrinkling and discoloring. In fact, the time period of this heat treatment was very long in comparison with real processing times.

The weight loss mainly originated from the loss of plasticizers and the solvent (MEK) used for film casting. The presence of plasticizers in the bottle formulation was determined in a previous study. Although the stabilizers were depleted by consumption during processing, the plasticizers were depleted by evaporation. Ulutan et al.¹² found that similarly plasticized nascent PVC-plastisol films lost a considerable

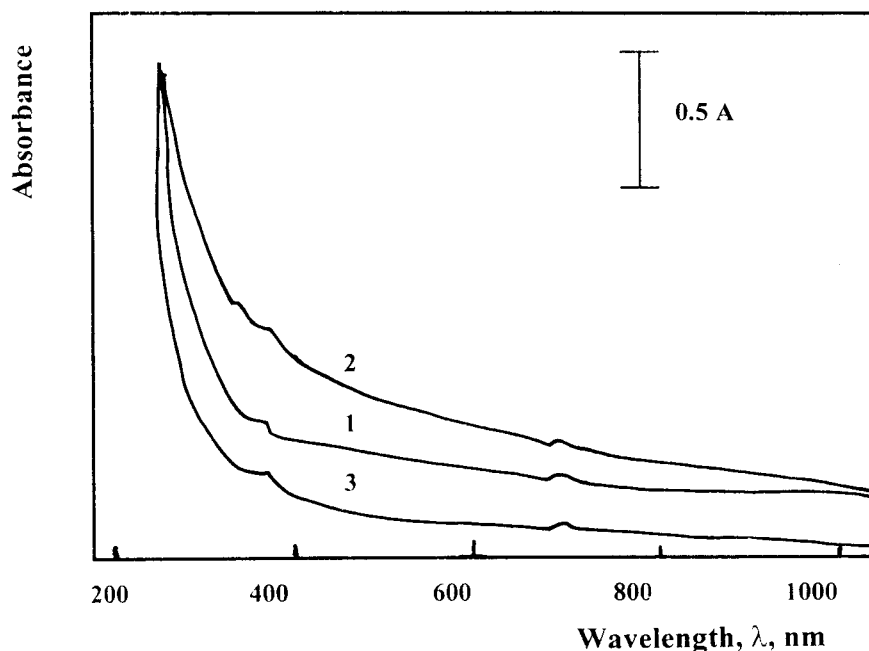


Figure 1 UV-vis spectra of films treated at 140°C: (1) no heat treatment, (2) heat treatment for 15 min, and (3) heat treatment for 30 min.

amount of plasticizer during gelling in a circulating air oven. When they compared films with the same surface area but with different thicknesses, they observed that the weight loss per unit of volume was higher in the thinner films. They suggested that this was likely due to a higher surface area susceptible to evaporation. They reported the total amount of the main evaporating species DOP and EPSO in their formulation to be 19.5 wt %.

The removal of hydrogen chloride resulted in the decomposition of PVC. Such structural changes were observed as polyene formation in the UV-vis spectra of the heat-treated films. Because similar bands were observed for different temperature treatments, the UV-vis spectra of the films treated at 140°C are depicted as examples in Figure 1. Polyene groups cannot be seen as separate peaks in these spectra. Nevertheless, PVC films with DOP and EPSO and similar com-

positions showed the same tendency of very high absorbance at about 200–330 nm.¹² However, the 600–1100-nm line in the UV spectra of DOP and EPSO was very flat and unlike those of recycled PVC films. Therefore, the increasing slope on the 330–1100-nm line suggested the formation of polyenes during the heat treatment of reformulated recycled PVC to a certain extent.¹² The absorbance values corresponding to certain polyenes (A_λ) were investigated, being divided by the 1100-nm absorbance (A_{1100}) to normalize the differences originating from the variations of the film thickness. The total absorbance ratios and the contribution of each polyene to the total absorbance ratio (as percentages) are reported in Table II. Each wavelength considered between 335 and 504 nm corresponded to a particular number of conjugated polyenes from 5 to 9 in increasing order. The polyenes observed at 335 and 360 nm were decapentanes and dimethyl dodeca-

TABLE II
Contributions of UV-Vis Absorbance Ratios (A_λ/A_{1100}) to the Total Absorbance Ratios and Initial Thicknesses of PVC Films Treated at Different Temperatures for Various Times

Heat treatment		Film thickness (mm)	% contribution of absorbance ratios to $\Sigma A_\lambda/A_{1100}$ ratio					$\Sigma A_\lambda/A_{1100}$
Temperature (°C)	Time (min)		335 nm	360 nm	415 nm	470 nm	504 nm	
—	0	123	29.37	23.42	18.73	16.25	12.34	99.16
140	15	138	31.97	22.13	17.21	14.75	13.93	100.99
140	30	138	29.10	22.75	18.52	15.35	14.28	144.14
140	45	70	32.63	24.82	17.73	13.12	11.70	503.51
160	15	110	35.29	24.89	16.18	12.44	11.20	182.59
160	30	245	48.36	24.94	11.20	9.90	5.60	400.81

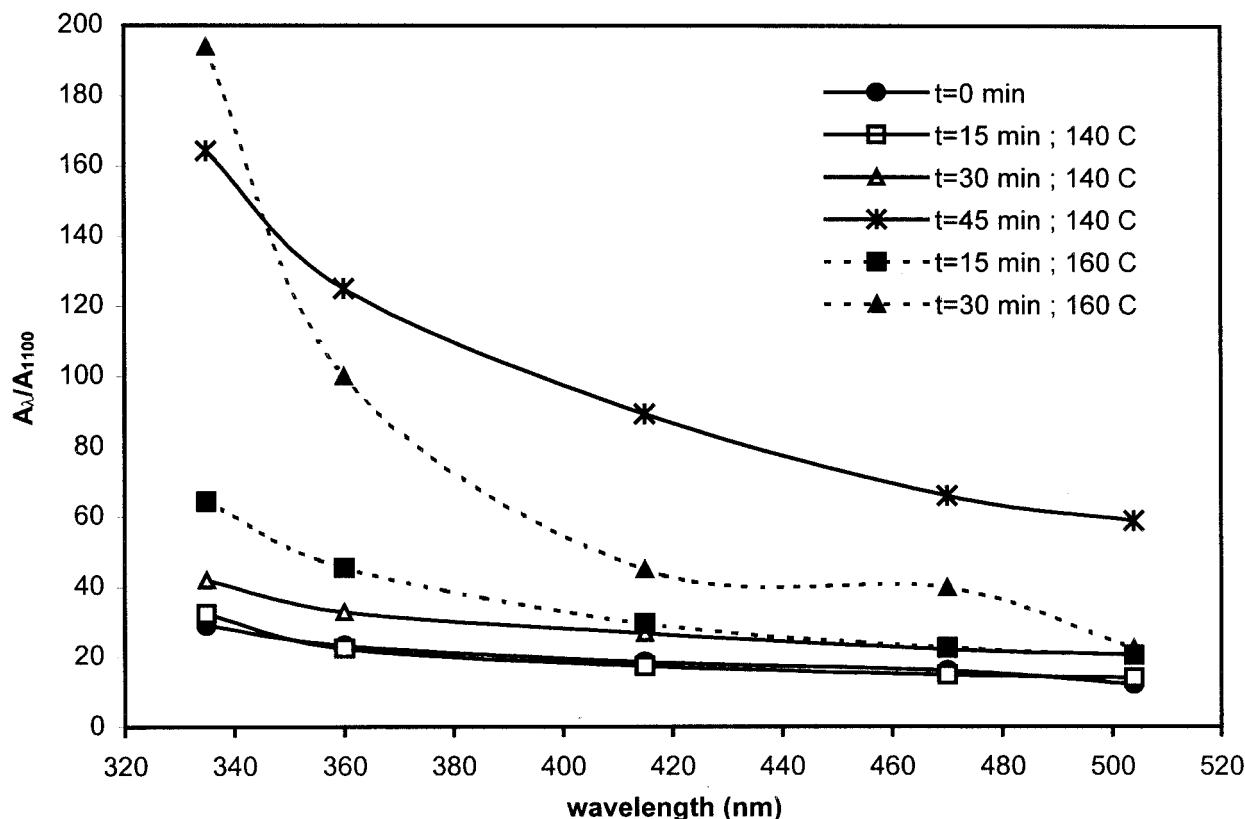


Figure 2 Relative UV absorbances of PVC films at several wavelengths for various heat treatments.

hexanes and had the lowest polyene numbers, with five and six $C=C$ groups, respectively. Longer polyenes with seven to nine polyene groups, that is, dihydro- β -carotene, lycopene, and dehydrolycopene, were observed at 415, 470, and 504 nm, respectively. As shown in Table II, each polyene provided an almost constant contribution to the total absorbance during mild heat treatments, which were thought to be equivalent to real processing conditions. This suggested that the polymer did not undergo severe decomposition, likely because of the positive effect of the stabilizers.

However, the distribution of the polyenes shifted toward the shorter sequences of polyenes at high temperatures and long times, as shown in Figure 2. A detailed explanation of why the temperature increase caused the polyenes to be shorter was given by Wypych.⁹ Briefly, the electronic structures, equilibrium geometries, and energy of the ground states of polyenyl cations and neutral polyenes affected this behavior.

The overall results suggest that acceptable structural changes occur under processing conditions appropriate for PVC, although values indicating strong decomposition were observed for severe treatments.

When high processing temperatures and long processing times are required, more efficient heat stabilizers should be used to prevent degradation. Because

of how the stabilizers are chosen, compatibility with the former stabilizers in the bulk material is important. Antagonistic effects among stabilizers are well known. Tin-based stabilizers are expensive. Lead-based stabilizers and heavy-metal stabilizers are not acceptable in short-life products for environmental reasons or in food applications for health reasons.

IR spectroscopy is also a useful tool for structural analysis. The IR spectra of films treated at 140°C are given in Figure 3. All the films showed similar structures in their IR spectra.

The bands attributed to the stearates and the bands related to degradation were investigated: 800–700- cm^{-1} twin bands, which were attributable to stearate type stabilizers,¹⁴ and 1570- and 1530- cm^{-1} bands, which were attributable to zinc and calcium stabilizers.¹⁵ To obtain a value consistent within the materials studied, we divided the peak height of each band by the film thickness to normalize the thickness effect. These values were proportional to the absorbance and were considered as a relative absorbance (Table III). A blue material that did not dissolve in the solvent showed a heterogeneous distribution within the film that likely resulted in some scattering of the absorbance values. However, the more severe the heat treatment was, the lower the peak height was. Moreover, the presence of those peaks even after heat treatments

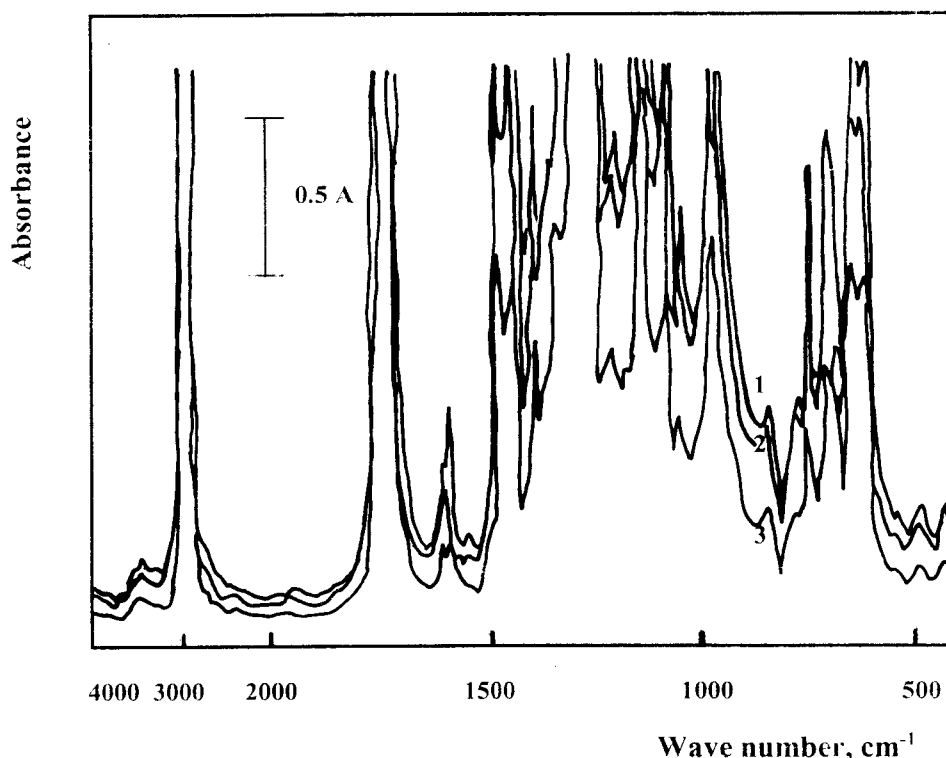


Figure 3 IR spectra of films treated at 140°C: (1) no heat treatment, (2) heat treatment for 15 min, and (3) heat treatment for 30 min.

indicated that the stabilizers were consumed were not yet used up.

The peak at 1700 cm^{-1} was attributed to the carboxylic acids formed by the evolved hydrogen chloride from PVC¹⁶ due to the thermal decomposition. However, it could not be evaluated because it overlapped with the peak at 1720 cm^{-1} , which was attributed to the esters in DOP and EPSO. Similar to their UV absorbance, the IR absorbance for DOP and EPSO was very high (1700 and 2950 cm^{-1}). Gökcel and Balköse¹⁷ reported an increase in the yellowness index with both the heating time and DOP concentration in PVC/DOP platelets. They observed through IR spectra that the thermal oxidation and volatilization of DOP occurred simultaneously with the dehydrochlorination of PVC upon the heating of the plastigels.

Particularly when there is not a sufficient amount of a heat stabilizer in a formulation, the higher the applied temperature is of the heat treatment, the larger the amounts are of carboxylic acids and hydroperoxides.¹⁸ The formation of hydroperoxides, which are found at 3400 cm^{-1} ,¹⁹ under a thermal treatment in air oxygen, shows almost no change with the temperature or heating time. Therefore, it suggests that there is no considerable decomposition.

DSC analyses also supported the IR evidence, showing that there was no considerable structural change upon the heating of the films. Moreover, zinc and calcium stearates, with melting points of 130 and 179–180°C, respectively,²⁰ were still present even after the severe treatments. These results proved that the added stabilizer mixture provided efficient stabilization and

TABLE III
Relative IR Absorbances of PVC Films with Various Heat Treatments

Heat treatment		Relative IR absorbance			
Temperature (°C)	Time (min)	700 cm^{-1}	800 cm^{-1}	1530 cm^{-1}	1570 cm^{-1}
—	0	5.04	2.28	1.06	0.41
140	15	5.80	2.81	0.81	1.28
140	30	5.38	2.47	0.76	1.24
140	45	6.56	3.01	0.67	0.83
160	15	5.99	2.88	1.18	0.85
160	30	2.31	2.88	1.80	0.53

that the amounts were sufficient to prevent the degradation of PVC upon reprocessing.

CONCLUSIONS

In this article, an appropriate thermal stabilizer system to be used for the processing of recycled postconsumer PVC water bottles has been proposed. These stabilizers, which account for environmental concerns, and plasticizers have been proven to be compatible with the pre-existing ones in the bottles. Although calcium and zinc stearates work well in combination with EPSO to prevent degradation, DOP is an adequate plasticizer for the makeup. The effectiveness of the makeup has been justified with spectroscopic, calorimetric, and weight-loss measurements after various heat treatments. Only after high-temperature treatments for long times has a small amount of decomposition been detected during UV and IR investigations. Therefore, the proposed formulation works well to prevent degradation and to compensate for the lost plasticizer.

Because the real processes applied to PVC are just above the fusion point and are slightly longer than the theoretical fusion time, the proposed reformulation will be satisfactory for preventing the degradation of PVC.

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