

Structural Changes and Mechanical Performance of Recycled Poly(vinyl chloride) Bottles Exposed to Ultraviolet Light at 313 nm

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ABSTRACT: The structural changes and mechanical performance of virgin poly(vinyl chloride) (PVC) bottle (VB) compounds blended with postconsumer PVC bottles collected from a specified factory (RB-F) and houses (RB-H), were examined before and after UV irradiation at 313-nm UV wavelength for different periods of time up to 28 days. The results indicated that, when exposed to UV light, the RB-F/VB blends containing greater conjugated double bonds with higher yellowness index appeared to exhibit better mechanical performance than that of the RB-H/VB blends. It was found that the amount of conjugated double bonds was not a linear function of the discoloration level of PVC compounds. Tensile strength of the VB compounds was not affected when incorporated with RB-F recycle, but

progressively decreased with increasing RB-H recycle. An optimum concentration for RB recycles to be added into the virgin compound was recommended for obtaining a maximum impact strength. Both tensile and impact strengths decreased with increasing UV exposure time, a severe degradation being obvious after a UV exposure time of 21 days. Hardness was not affected significantly by the addition of PVC recycle, but increased with increasing UV exposure time. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 84–94, 2004

Key words: poly(vinyl chloride); photochemistry; recycling; extrusion; FTIR

INTRODUCTION

Over the past decades, polymeric materials are increasingly in demand because of their applications and performance, this being one of the main reasons that higher quantities of polymeric waste are produced. Construction and packaging have been found to constitute the greatest part of domestic wastes.^{1,2} In these applications, poly(vinyl chloride)s (PVCs) are included. The volume of PVC scraps, produced by both manufacturers and consumers each year, to be recycled, is so large that numerous alternative recycling technologies have become necessary. The recent status of recycling PVC has been reviewed by many researchers.^{3–6} Recent work by Sombatsompop et al.^{7–8} investigated the possibility of recycling PVC pipes and bottles by adding the recycles in various concentrations into different PVC virgin compounds,

and the data on rheological, morphological, mechanical, and thermal properties of the blends were then reported and discussed. The work recommended that the concentrations between virgin and recycled materials to be used be different, depending on the properties investigated, chemical compositions in the compounds, and the type of recycled grades (whether they were pipes, bottles or, cables). In addition, some properties such as tensile strength and impact strength could be improved by incorporating recycled PVC.

During service use, PVC products can be attacked by UV light at wavelengths greater than $\lambda > 250$ nm. These wavelengths have sufficient energy to cleave the C—Cl bond, which has a bond energy of 325 kJ mol⁻¹, resulting in a degradation of PVC compounds.⁹ The degradation of PVC can proceed by a dehydrochlorination process, which gives rise to the formation of long conjugated double bonds or polyene sequences $(-\text{CH}=\text{CH}-)_n$, which are responsible for the discoloration of the irradiated PVC products. In the presence of oxygen, an oxidation reaction can develop simultaneously with the dehydrochlorination, causing formation of carbonyl groups in the PVC chains that in addition suffer cleavages and crosslinking.

A number of studies^{10–13} have reported on the photodegradation of PVC. Torikai and Hasegawa¹⁰ examined the degradation of waste plastics materials under

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TABLE I
Material Characteristics and Sample Codes

PVC material (grade and supplier)	Code	Material compositions (pph)
Virgin PVC Bottle Grade (B0504BLA). In granule form by Thai Unions Co. Ltd. (Bangkok, Thailand)	VB	1.6 of liquid thiotin (stabilizer) 12.0 of MBS (impact modifier) 2.0 of processing aid (acrylic type) 1.5 of fatty acid
Processed PVC flakes (collected from factory) by Thai Unions Co. Ltd. (Bangkok, Thailand)	RB-F	Unknown
Recycled PVC flakes (collected from postconsumers)	RB-H	Unknown

terrestrial sunlight focusing on the effect of preirradiation with short-wavelength UV radiation on the structural change of PVC through gel permeation chromatography (GPC). It was found that both main-chain scission and degraded PVC formation were accelerated by preirradiation, the effect varying with preirradiation time. Rao et al.¹¹ studied microstructural changes during photodegradation of PVC by varying UV wavelengths using ¹³C- and ¹H-NMR spectroscopy. It was found that the rate of dehydrochlorination increased with increasing dosage of UV radiation. The degradation was minimized by adding dibutyl tin dilaurate (DBTL) stabilizer. Anton-Prinet et al.¹² studied the carbonyl and polyene indices of PVC samples that were exposed to accelerated ageing at varying UV intensity and temperature. They found that the thickness of the oxidized layers that were determined by carbonyl profiles tended to increase with increasing ageing temperature. The thickness of polyene sequences decreased with UV light intensity, but increased with temperature. Veronelli et al.¹³ studied thermal dehydrochlorination of PVC compounds under accelerated weathering under nitrogen conditions at a temperature of 180°C and determined the amount of eliminated HCl and the kinetics of photooxidation using UV-vis spectroscopy. The results suggested that the presence of long sequences of conjugated double bonds occurring in the compound did not influence the mechanism of the photodegradation of the PVC chains.

A large number of studies has been published on the effects of UV light on the properties of virgin PVC compounds, but very few have examined recycled PVC compounds in contact with UV light. This is because of the difficulties in controlling the initial properties of the recycled PVC products, whose contents (or ingredients) are usually inconsistent and are greatly dependent on the sources and types at which the recycled PVC is collected. However, experimental data of UV light effects on the property changes of recycled PVC would be very useful for PVC industries because now many PVC products are increasingly being fabricated by incorporating recycled PVC for cost-saving purposes. As a consequence, it seems of

importance for this study to quantitatively examine the effects of UV light on changes in structural and mechanical properties of blends of virgin PVC compounds and recycled or processed PVC bottles, which were collected from two different sources (specified factory and household). The parameters of interest included polyene and carbonyl indices, yellowness index, tensile and impact strengths, and hardness property.

EXPERIMENTAL

Raw materials

This work used three different PVC compounds, whose details and sample codes are listed in Table I. It should be noted that the recycled PVC bottle flakes (RB-H) were collected from postconsumers, whereas the processed PVC flakes (RB-F) were obtained from a specified factory during the action of the pinch-off in the (blow-molding) process. PVC flakes were washed with utmost care to remove any contaminants, and finally granulated to give recycled PVC flakes before further use. The recycled PVC bottles were incorporated into a virgin PVC bottle compound that was coded as "VB." The original compounds used to produce the RB-F flakes were the same as the VB compound.

Experimental design and PVC blending

The materials used in this work were derived from the blending of the recycled or processed PVC flakes into virgin PVC bottle compounds at different concentrations ranging from 0 to 100 wt %. The work was conducted in two different systems: (1) adding RB-F into VB and (2) adding RB-H into VB. The recycled and processed PVC flakes were granulated in a granulator (2835 Bosgo Engineering Co. Ltd., Germany) before dry-blending with virgin PVC to the required compositions, using a twin-screw extruder manufactured by Haake Co. (Bersdorff, Germany). The head of the extruder contained a three-strand die (each strand having a diameter of 3 mm), which produced three

extrudates at the die exit. The dry-blend compounds were then passed through a water bath by the use of a pull-off unit before undergoing a pelletizer to produce blended granules. Thereafter, the blended granules were refeed into the extruder using a slit die having width \times height \times length of $18.2 \times 2 \times 16 \text{ mm}^3$ to produce slit extrudates as test pieces for UV ageing and mechanical tests. The screw rotating speed was 100 rpm with the barrel temperature setting on zone one (near the hopper) being at 140°C , on zone two at 150°C , and on the die at 160°C .

UV light exposure

The PVC test pieces from both systems were used, in both granular and test-piece forms, to evaluate the structural and property changes before and after undergoing UV light at different exposure times (from 0 to 28 days) using a Q-UV apparatus with UV-B neon fluorescence lamps emitting a spectrum at a wavelength of 313 nm. The exposure temperature in the apparatus was controlled at 60°C . It should be noted that all the samples were kept and UV-degraded in the UV apparatus at the same time, the samples being taken out periodically at required UV exposure times for further characterizations.

Characterization

FTIR analysis

To assess the extent of degradation of the PVC compounds, the quantities of conjugated double bonds (or polyene sequences) and carbonyl groups were determined by infrared analysis using a Thermo-Nicolet Nexus 470 FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI). Details of the sample preparation and measurement were reported in previous work.^{7,14} For a given test condition, five samples were used to produce an average value of the results, and the average repeatability errors were calculated to be $\pm 1.5\%$, the calculation of the repeatability errors being found elsewhere.¹⁵

Tensile, impact, and hardness tests

The tensile test was performed following ASTM D 638 (1990), on a Hounsfield (QMAT 1.23) tensile testing machine at a crosshead speed of 50 mm min^{-1} . The Izod impact tests were carried out, according to ASTM D256 (1990), on a Ceast Impact Tester with the notched side facing the pendulum. The hardness was evaluated using a Durometer Shore D (Model 409) supplied by PTC Instruments Co., the test procedure being specified by ASTM D2240 (1990). Five test pieces

were used to generate an average value for each mechanical test for a given test condition, and the average repeatability errors were calculated to be $\pm 2.7\%$.

Discoloration test

The color changes of the blended compounds were determined using a DataColor CIE-LAB System (GretagMacbeth; Color-Eye 3100, Regensdorf, Switzerland), which computed color differences between the measured compound and the control compound under normally visible light (D65). Only the blue-yellow zone was of interest in this work. The results obtained were based on the measurement of a yellowness index (YI), expressed as follows:

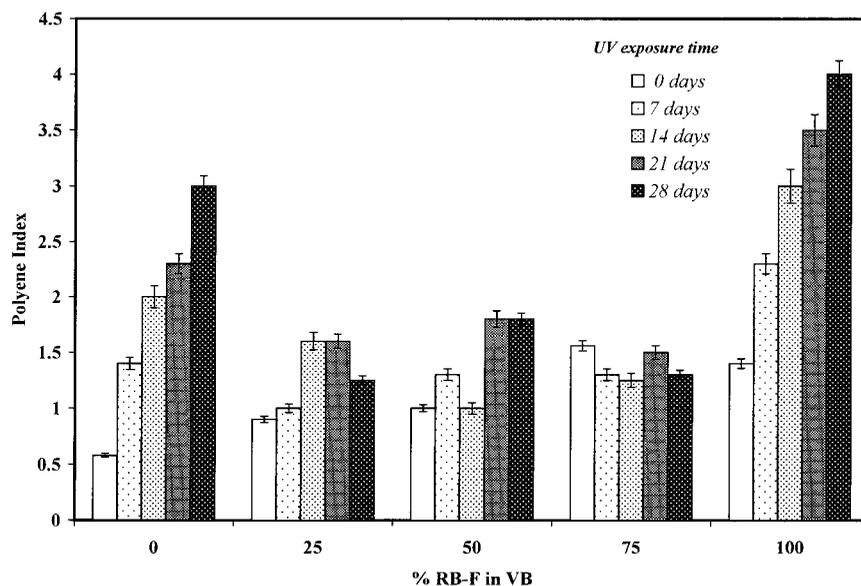
$$YI = \frac{100(1.28X_{\text{CIE}} - 1.06Z_{\text{CIE}})}{Y_{\text{CIE}}}$$

where X_{CIE} , Y_{CIE} , and Z_{CIE} are transstimulus values of the specimens. A positive yellowness index describes the presence and magnitude of yellowness, and samples with a negative yellowness index will appear bluish. The test procedure was specified by ASTM D1925 (2000).

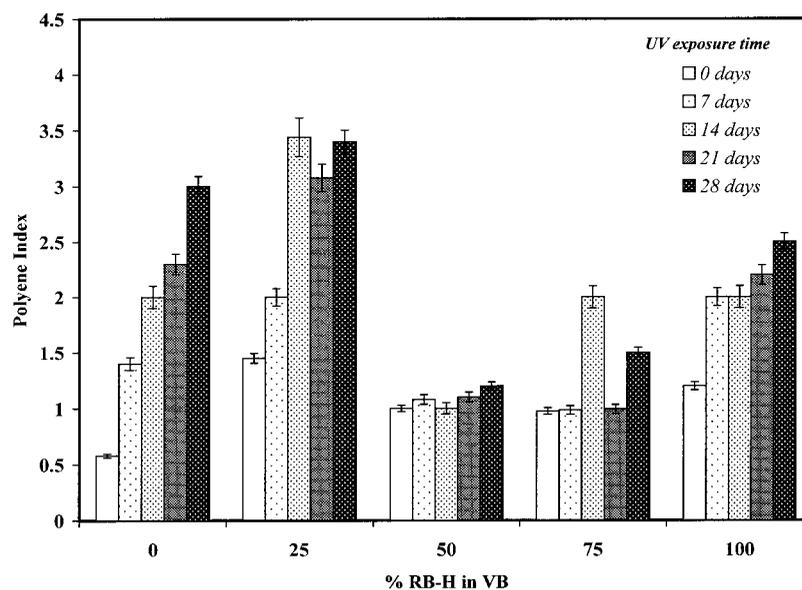
RESULTS AND DISCUSSION

Structural changes

Figure 1(a) and (b) show the effect of incorporation of RB-F and RB-H recyclates into VB compounds on conjugated double bonds or polyene index for different UV exposure times, respectively. It can be seen that at 0 days, the addition of RB-F into VB compounds generally tended to give slightly higher values of polyene sequence, except for the 25% RB-H in VB compound. Considering 100% RB-F and RB-H samples, it was found that without UV light, the polyene indices for these two recyclates were quite similar. After being exposed to UV light, the rate of polyene sequence production for RB-F was greater than that for RB-H. This was interesting and it may be the reason that the RB-F/VB blends had a greater polyene index than that of the RB-H/VB blends for any given recyclate concentration. In general, one may expect to obtain a greater polyene content in RB-H because the RB-H probably had more thermal and/or UV history during service, although this was not the case. The higher production rate of conjugated double bonds in RB-F may be associated with two synergetic factors: (1) the presence of carbonyl groups (which are usually present as impurities in processed PVC), and (2) the amount of allylic chlorine atoms per PVC molecular chain of RB-F and RB-H recyclates.



(a)



(b)

Figure 1 Effect of addition of recycled PVC bottles into VB compound on polyene index for different UV exposure times: (a) RB-F in VB; (b) RB-H in VB.

1. *The presence of carbonyl groups.* Because this work was carried out with the presence of oxygen, the compounds were entitled to oxidation reaction, which developed simultaneously with the dehydrochlorination reaction with formation of carbonyl groups on the polymer chains. Work by Decker⁹ clearly stated that carbonyl groups in PVC chains could act as sensitizers for accelerated production of polyene sequences. Figure 2(a) and (b) indicate that the quantity of carbonyl groups in RB-F was greater than that in RB-H. This may be one of the reasons for increasing the

production rate of polyene sequences in RB-F/VB blends. The results also indicated, as one would expect, that the longer the UV exposure time, the higher the quantity of carbonyl groups in PVC molecules.

2. *The amount of allylic chlorine atoms.* In this case the RB-F recycle was thought to have more allylic chlorine atoms per PVC molecular chain than RB-H recycle, which can easily initiate a zip-dehydrochlorination reaction under UV-light exposure. This was considered to be the case based on two independent thermal tests, which were

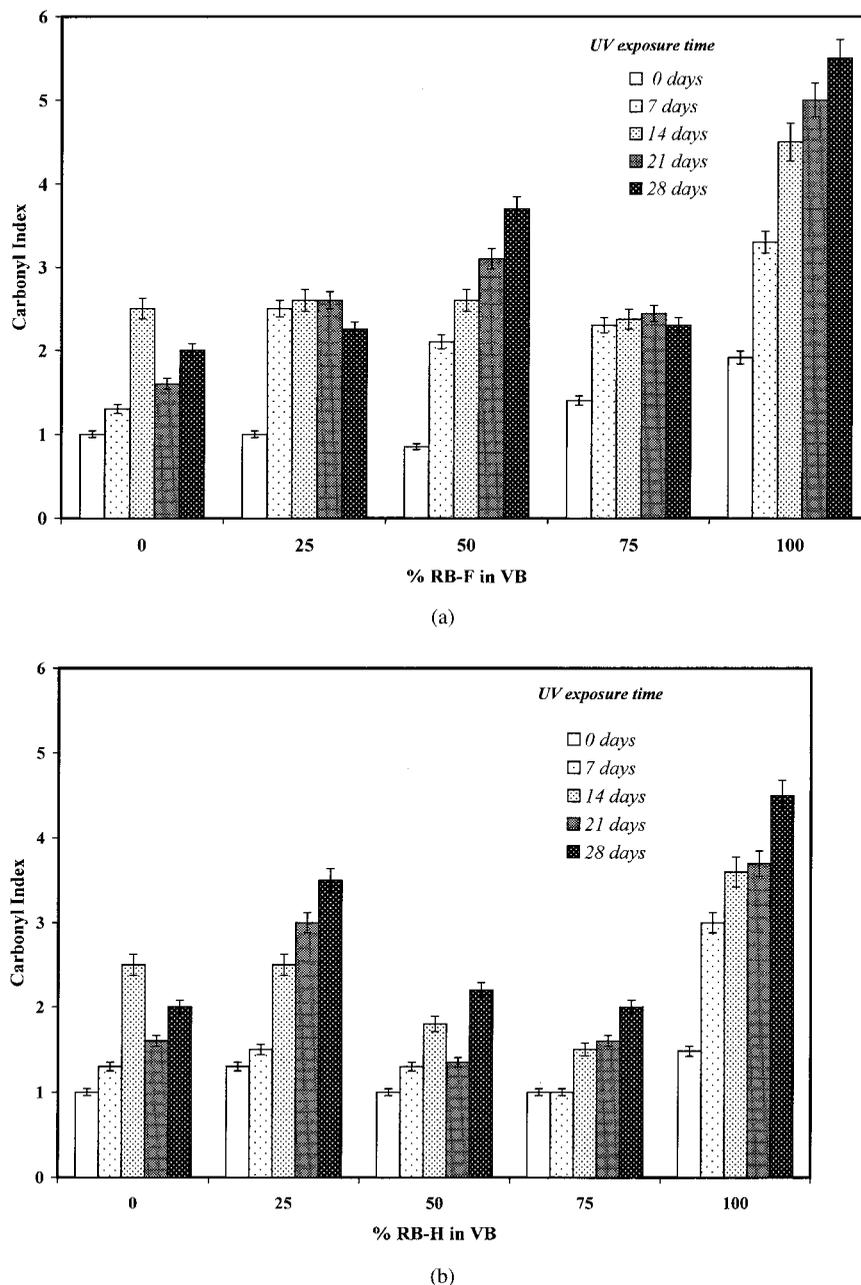


Figure 2 Changes in carbonyl groups in recycled PVC bottles blended with VB compound for different UV exposure times: (a) RB-F in VB; (b) RB-H in VB.

DSC and TGA tests used for determining the glass-transition temperature and the quantity of liberated CI atoms in RB-F and RB-H recyclates, respectively, results of which are shown in Table II. It can be seen that the glass-transition temperature for RB-F (82°C) was greater than that for RB-H (73°C), whereas these two recyclates had relatively the same value of %CI atoms. Because the materials used in this work were not virgin, the CI atoms in the compounds were possibly in the form of allylic chlorine atoms. The results from both tests implied that RB-F recyclate had a

TABLE II
Glass-Transition Temperature and %CI Content of RB-F and RB-H Recyclates

PVC recyclate	Glass-transition temperature ^a (°C)	CI content ^b (%)
RB-F	82	57
RB-H	73	56

^a From a Perkin-Elmer DSC-7 instrument with a heating rate of 10°C/min.

^b From TGA Instruments (TGA-2950) with a heating rate of 10°C/min.

greater weight-average molecular weight, and contained a higher number of allylic chlorine atoms per PVC molecular chain than RB-H recycle before exposure to UV light. If this were the case, the zip-dehydrochlorination reaction in the PVC molecular chains would become accelerated. Decker⁹ clearly suggested that the main cause of the great sensitivity of PVC to UV light originates from the presence of allylic chlorines. In relation to this work, the amount of conjugated double bonds in RB-F was greater than that in RB-H. Therefore, the RB-F/VB blends had a greater polyene index than that of the RB-H/VB blends for any given recycle concentration. This may also be the reason that the polyene index of the VB compound with 25% RB-H had an exceptionally high polyene value, as mentioned earlier.

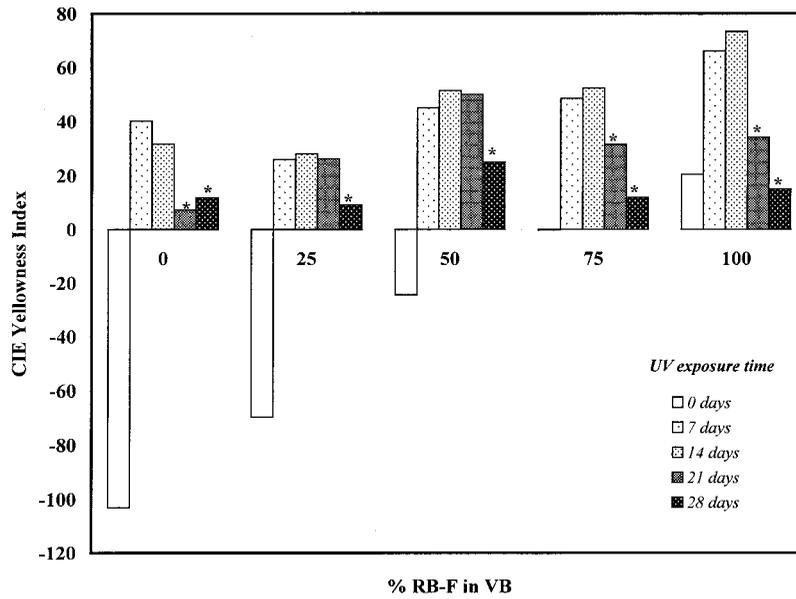
Considering the effect of UV exposure time, it was found that the longer the UV exposure time, the higher the polyene contents formed. This has been well documented that the C—Cl bonds in PVC molecules can be cleaved by UV light, which then produce polyene sequences in the main chains. The effect was more obvious for RB-F, the reason for which was linked with the quantities of carbonyl groups and allylic chlorine atoms as discussed earlier.

The results of the polyene index can be substantiated by color changes in PVC compounds because it is widely accepted that long conjugated polyene sequences, which arise from the intramolecular chain dehydrochlorination, are responsible for the discoloration of the irradiated PVC products.^{16,17} The greater the polyene sequences, the yellower the compound.¹⁷ The discoloration of PVC blends is monitored in terms of the CIE yellowness index, as shown in Figure 3(a) and (b). Samples with positive yellowness index indicate the presence and magnitude of yellowness, and samples with a negative yellowness index indicate bluish. It can be seen that before undergoing UV light, RB-H/VB blends tended to turn yellow with a lesser amount of recycle than RB-F/VB compounds, for given recycle content and UV exposure time, although the polyene index in RB-F was greater. These results suggested that the amount of polyene sequences was not a linear function of the degree of PVC discoloration. This involved the formation rate of polyene sequences in RB-F, which was comparatively greater. It was also noticeable that all PVC samples turned yellow right away after 7 days of UV light, and the yellowness index changed slightly at 14 days. It should be noted that the samples at UV exposure times of 21 and 28 days, showing a sudden decrease in CIE yellowness index, exhibited a dark brown color, which clearly suggested a severe UV degradation had occurred in the PVC compounds.

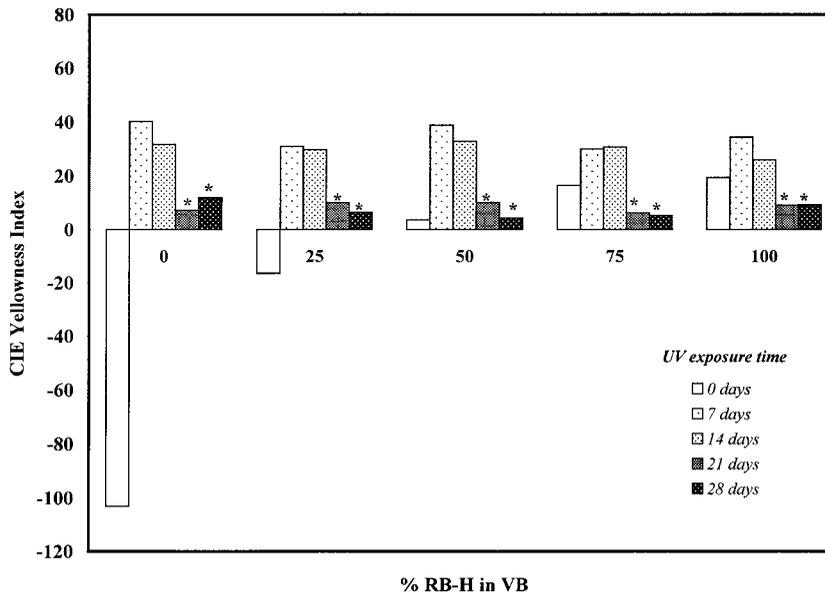
Mechanical performance

The mechanical performance of recycled PVC products blended with virgin PVC compounds was assessed in terms of ultimate tensile strength, impact strength, and hardness. Figure 4(a) and (b) show the effect of additions of RB-F and RB-H recyclates into VB compounds on ultimate tensile strength for different UV exposure times. It can be seen that the RB-F/VB blends seemed to have greater tensile strength than that of RB-H/VB for all RB concentrations. The tensile strength for VB compound did not change significantly with addition of RB-F recyclates, which was attributed to the fact that the RB-F and VB compounds were of the same material as mentioned earlier. In this case, the homogeneity of RB-F/VB was likely better than that of RB-H/VB. For RB-H/VB blends, the tensile strength progressively decreased with increasing RB-H content. This was attributed to a dilution effect. The RB-H recycle itself had a low tensile strength. Therefore, adding RB-H would reduce the tensile strength. In addition, as RB-H recycle was collected from used PVC bottles, the compound may have been contaminated by impurities (such as plastic or/and paper labels), which could have acted as defects in the RB-H/VB blends. Work by Arnold⁶ indicated that most impurities in recycled PVC products were usually polyolific materials that could cause some structural changes in PVC compounds, especially under melt-blending conditions. The greater the RB-H content, the greater the defects in the RB-H/VB blends, and thus the decreased tensile strength. Our previous work¹⁴ also suggested that the presence of polyethylene in PVC compounds could alter the molecular structure of PVC, which was derived from a grafting of PE and PVC macroradicals during a melt-blending process.

Considering the effect of UV exposure time, it is noticeable that the tensile strength increased slightly after experiencing UV light for 7–14 days, and then started to decrease at longer UV exposure times (21 and 28 days). The increase in tensile strength at low UV exposure times (7–14 days) may be associated with the increase in polyene content, which would lead to an increased stiffness of the PVC. It should be noted that a reduction of percentage elongation of the samples was observed during the tensile experiment (results not shown) after experiencing 7–14 days of UV light. After 14 days of UV exposure time, excessive polyene sequences were produced and this probably gave rise to a severe degradation (compounds at this stage exhibited a dark brown color, as already discussed with respect to Fig. 3). The degradation probably caused main chain scissions of PVC, and the tensile strength therefore decreased.⁹ Having considered the changes in conjugated double bonds of polyene (Fig. 1) and tensile properties (Fig. 4) between



(a)



(b)

Figure 3 CIE yellowness index of recycled PVC bottles blended with VB compound for different UV exposure times: (a) RB-F in VB; (b) RB-H in VB.

RB-F/VB and RB-H/VB blends, it can be suggested that PVC compounds with higher conjugated double bonds may not necessarily have lower mechanical properties than those with lower conjugated double bonds.

Impact strength values of VB compounds blended with RB-F and RB-H recyclates are shown in Figure 5(a) and (b), respectively. It may be observed that RB-F/VB blends generally had greater impact strength than that of RB-H/VB blends, especially at higher RB loadings. This was not surprising given that

the RB-H recyclates had been collected after practical usage, and some additive materials (such as plasticizers, stabilizers, and impact modifiers) in the compound may have volatilized during processing, leading to a compound with lower impact strength. For a given UV exposure time, the impact strength of most RB-F/VB samples increased up to a certain concentration of RB-F and then started to decrease at higher RB-F loadings. In the case of RB-H/VB, the impact strength decreased with increasing RB-H content. The increase in impact strength was probably caused by a

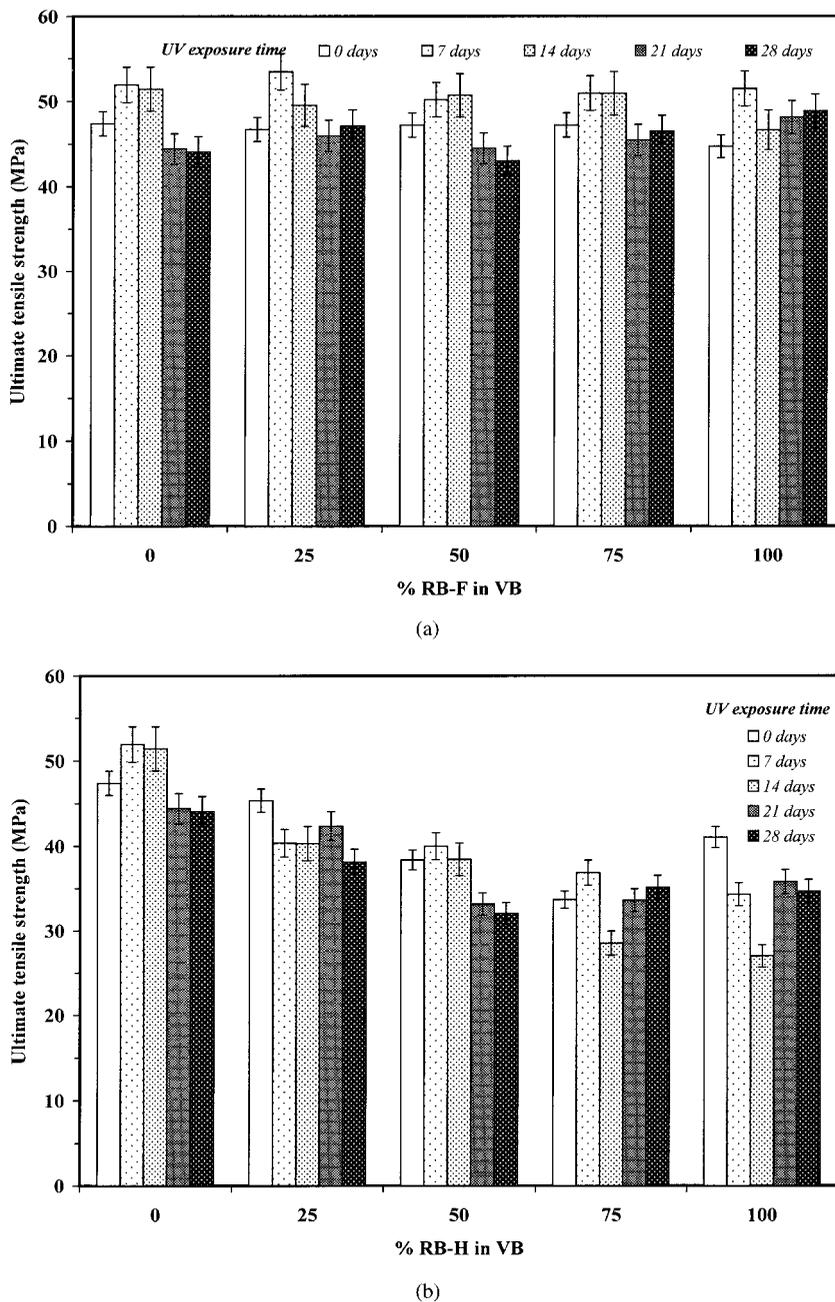
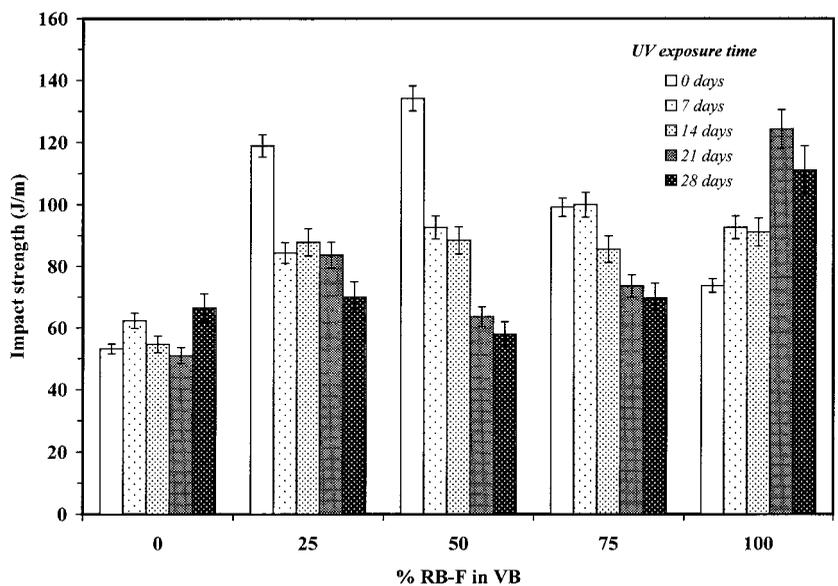


Figure 4 Effect of addition of recycled PVC bottles into VB compound on ultimate tensile strength with different UV exposure times: (a) RB-F in VB; (b) RB-H in VB.

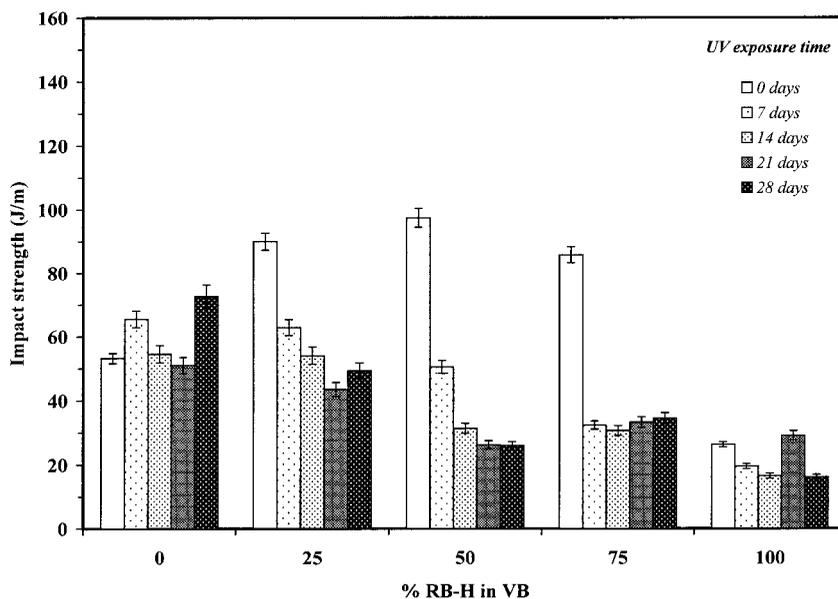
gelation effect as a result of the use of reprocessed PVC compounds (RB-F in this case). The decrease in impact strength at higher RB-F loading was associated with two reasons: (1) a too high gelation level,¹⁸ and (2) the loss of volatile additives in the PVC compounds. The latter reason may have resulted from either the use of postconsumer PVC recycle or a too high level of recycled PVC material used.⁵ The impact strength results evidenced in this work were in good agreement with those found in previous work⁷ that investigated the effect of the addition of recycled PVC

pipe into virgin PVC compounds (both bottle and pipe grades) on impact strength.

Figure 5(a) and (b) also show the impact strength of PVC blends for different UV exposure times. It is noticeable that longer UV exposure times tended to lower the impact strength for both RB-F/VB and RB-H/VB blends. This was expected, given that longer UV exposure times caused an acceleration of the dehydrochlorination reaction, which produced higher numbers of polyene sequences (C=C). The presence of polyene sequences led to an increase in embrittle-



(a)



(b)

Figure 5 Impact strength of recycled PVC bottles blended with VB compound for different UV exposure times: (a) RB-F in VB; (b) RB-H in VB.

ment (reduced impact strength) of the molecular chains. This was in good agreement with the work by Scott and Tahan.¹⁹

The hardness of all PVC blends may be observed in Figure 6(a) and (b) to increase significantly with exposure to UV light at an exposure time of 7 days, but the effect became less pronounced for longer UV exposure times. The increase in hardness of the blends was probably attributed to the production of carbonyl groups in the PVC compounds as discussed with respect to Figure 2. This explanation was also evidenced by Scheirs,¹⁷ who suggested that the presence of car-

bonyl groups in a PVC compound could result in an increase in density and hardness of the compound.

CONCLUSIONS

Postconsumer PVC bottles and processed PVC scraps were introduced into virgin PVC bottle compound and the structural and mechanical property changes were examined. The following can be noted:

- The RB-F/VB blends were found to produce a higher quantity of conjugated double bonds with

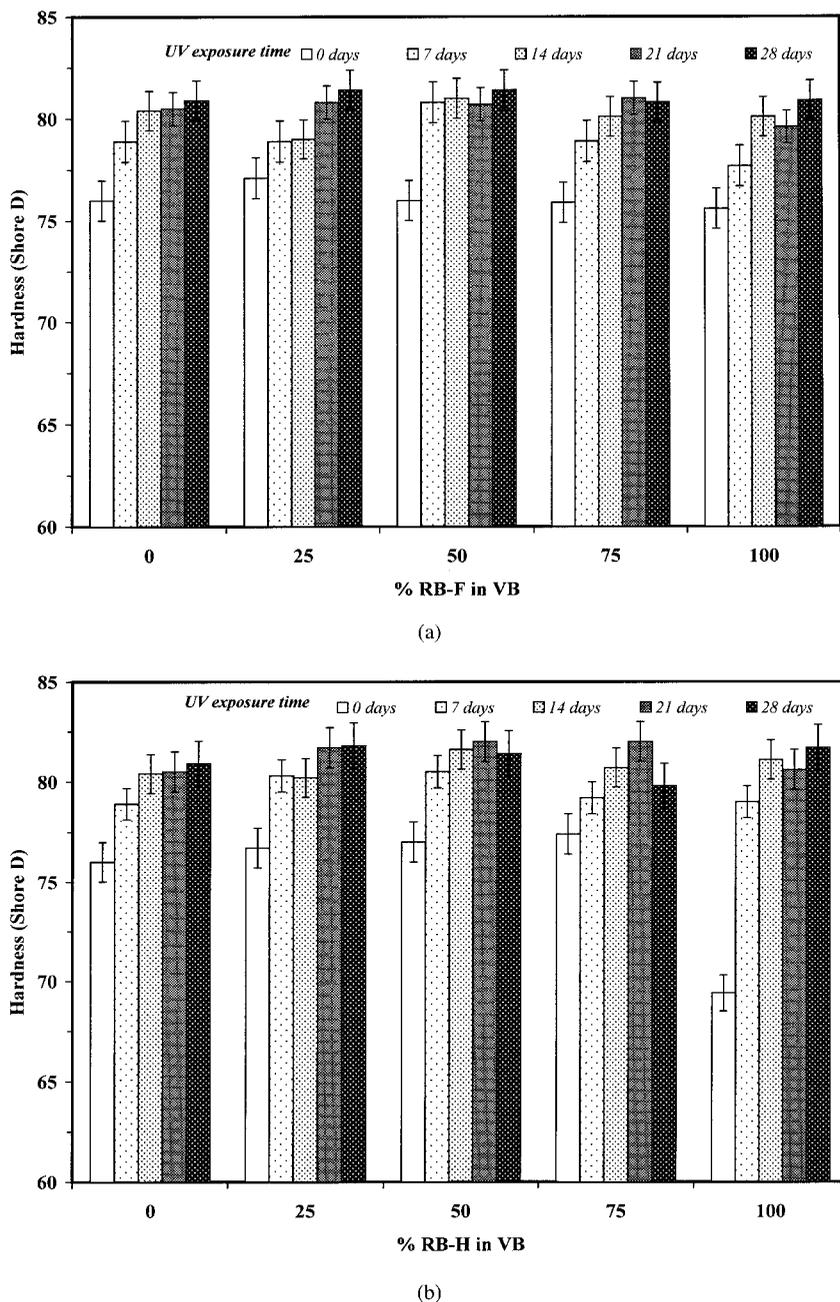


Figure 6 Effect of addition of recycled PVC bottles into VB compound on hardness with different UV exposure times: (a) RB-F in VB; (b) RB-H in VB.

greater yellowness index when exposed to UV light than RB-H/VB. This involved the presence of carbonyl groups and the number of allylic chlorine atoms per molecular chain of PVC, which resulted in an acceleration of a zip-dehydrochlorination reaction.

- Tensile strength of the VB compound was not affected when incorporated with RB-F recyclate, but progressively decreased with RB-H recyclate, which involved homogeneity of the blends and the impurities in the recyclates. Impact strength of

the VB compound was found to increase by adding RB recyclates up to a certain concentration, and then decrease at higher recyclate loadings. Both tensile and impact strengths were observed to decrease with UV exposure time, a severe degradation of PVC blends being clearly visible after being exposed to UV light for 21 days.

- RB-F/VB blends were observed to exhibit higher mechanical performance than that of RB-H/VB blends, although they produced a greater amount of conjugated double bonds with higher yellow-

ness index. This finding suggested that the amount of polyene sequences was not a linear function of the level of discoloration of PVC compounds.

- Hardness was not significantly affected by the addition of PVC recycle, but increased with increasing UV exposure time because of the increased production of carbonyl groups.

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