Mechanical Recycling of Post-Used HDPE Crates Using the Restabilization Technique. II: Influence of Artificial Weathering

C. N. KARTALIS,[1] C. D. PAPASPYRIDES,[1] R. PFAENDNER,[2] K. HOFFMANN,[2] H. HERBST[2]

[1] Laboratory of Polymer Technology, Department of Chemical Engineering, National Technical University of Athens (NTUA), Zographou, Athens 157 80, Greece

[2] Ciba Spezialitätenchemie Lampertheim GmbH, Chemiestrasse, D-68623 Lampertheim, Germany

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ABSTRACT: Artificial weathering was applied for about 8000 h to evaluate the light stability of postconsumer high-density polyethylene (HDPE) material recycled from bottle crates. For recycling the remelting-restabilization technique was applied. To study the effect of the restabilization, the tensile impact strength was monitored during the artificial weathering exposure. The data were compared with microphotographs of the specimens' surface. Repigmentation was used to evaluate the role of new pigments on the final performance of the recycled material. The repigmented grades were further studied by colorimetric determinations of the color difference (ΔE) during artificial weathering. The results illustrate that the restabilization is mandatory for improving the light stability of the postconsumer crate material, ensuring its re-use in the original application. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1118–1127, 2000

Key words: plastics recycling; restabilization; artificial weathering; light exposure; HDPE; bottle crates

INTRODUCTION

Mechanical recycling of plastics is one of the preferred recycling options, for ecological, economical, and in particular energetic reasons.[1–5] However, the advantages and ecological benefits of material recycling are especially proven if virgin material can be substituted by recyclates. Consequently the recyclate has to fulfill the same function as virgin material with respect to performance, mechanical, and visual properties and durability. These high-value recyclates with properties close to virgin material can only be achieved by carefully controlling the quality and upgrading of the recyclate. At the same time economical success of mechanical recycling will be gained by creating high-value products.[5–7] Therefore, it is essential to investigate the quality of recyclate streams and to show efficient ways to upgrade recyclate to the properties of virgin plastics.

The quality of the post-used material intended for reuse is determined by the history of the polymer synthesis, the previous processing steps, the final application, as well as the additives, the residual stabilizer content, and finally the extent of contamination by impurities.[1,2] In the present material stream of high-density polyethylene (HDPE) bottle crates the level of impurities from other polymers and contamination from contact media can be neglected. In this case the decisive factors for the resulting material properties are

Correspondence to: C. D. Papaspyrides.

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the residual stabilizer content and the predegradation during first life.

During previous processing steps, plastics undergo irreversible changes leading to preliminary molecular damage, such as chain scission, cross-linking, or formation of double bonds. Additionally, during their service life, plastics suffer from natural aging mainly caused by oxidation and/or photo-oxidation, leading to deterioration of the mechanical properties.[3,4,8–11]

Polymers are markedly susceptible to oxidative deterioration when exposed to sunlight. The absorption of light depends mainly on the polymer structure. For example, saturated hydrocarbons such as polyolefins, which are simply long-chain alkanes, do not absorb above 250 nm, well below the UV-part of sunlight (≍ 290–400 nm), which reaches the earth's surface. They can, however contain many fortuitous or deliberately added UV-light absorbing species (chromophores) that shift the absorption to a longer wavelength. The main chromophores are pigments, additives, impurities, and catalyst residues, or products from oxidation during processing and use, such as carbonyl groups, double bonds, and hydroperoxides. During the photo-oxidation, free carbon radicals ($R^{\bullet}$) are formed in the polymer by excitation of absorbing chromophore groups, which rapidly combine with oxygen to give peroxy radicals ($ROO^{\bullet}$). These radicals react quite slowly by hydrogen abstraction from C-H sites on the backbone to generate hydroperoxide groups (ROOH) and new carbon-centered radicals, which restart the photo-oxidation cycle. Hereby, during this cycle, the progressive polymer modifications by chain scission or cross-linking result in crack formation in the surface zone and in an associated decrease of the mechanical performance.[7,12,13]

The described photo-oxidation mechanism offers a number of possibilities to avoid or retard the cascade by stabilization. However, in the case of recyclates, the original stabilization is depleted during the primary conversion process and first service life and in this way it becomes insufficient to protect the polymer from light attack during its second life. The effect of insufficient protection of the polymer can be highly detrimental to the long-term durability of the recycled material. The latter means that the recycled product would be quite unsuitable for any long-term outdoor application.[1,2,10,14]

Restabilization, the upgrading method of the postconsumer plastic material by processing, heat, and light stabilization, can equalize or at least reduce the UV light influence to such an extent that the required long-term stability is generated. As a result, the value of the recycled end product is increased.[1,2,6,7]

Conventional oven tests, Weather-O-Meter tests, and outdoor aging are applicable for the assessment of the resistance against heat aging or weathering and its enhancement by restabilization.[1,2] Particularly in the case of photo-oxidation, natural or outdoor weathering can take years before it becomes possible to collect useful results. Thus, increasing need has arisen for reliable predictions of outdoor lifetime through accelerated or artificial weathering tests. Numerous lamps of various types have been considered so far as sources of UV light-accelerated polymer degradation. Dealing with HDPE good correlation has been found between natural weathering and xenon arc Weather-O-Meter artificial exposure.[15,16]

In the past, Vink et al.[17] studied the effect of various UV stabilizers added to degraded, yellow-pigmented, HDPE material originating from crates used for 10–13 years. Outdoor and Xenon-test-1200 tests proved that the UV stability of the degraded crate material could be considerably improved by remelting and restabilization using a Hindered Amine Stabilizer (HAS), Tinuvin 770, from Ciba Specialty Chemicals Inc., Lamperthe, Germany. In another work, Ciba Specialty Chemicals Inc. studied the restabilization effect on the light stability of 100% recyclate from 5 year old bottle crates, during Florida weathering exposure. The results showed that the light stability of the aged crate material was improved by means of the aforementioned hindered amine stabilizer and also by a benzotriazole UV absorber.[1,18] Recently, the same company introduced a new restabilization system, Recyclossorb 550, a combination of processing and light stabilizers, especially developed for recycling of polyolefins from/for outdoor applications. For example, artificial weathering of blue pigmented, post-used, HDPE crates showed that restabilization with Recyclossorb 550 maintains the material properties on a very high level over 6000 h xenon exposure.[7]

Despite several publications showing the benefits of upgrading recyclates by stabilizers there is a lack of fundamental investigations on all important parameters such as processing,[19] weathering (this paper), and aging[20] combined in addition with repigmentation. In particular, in a previous study carried out at National Technical University of Athens and Ciba Spezialitätenchemie Lampertheim GmbH, the influence of reprocess-

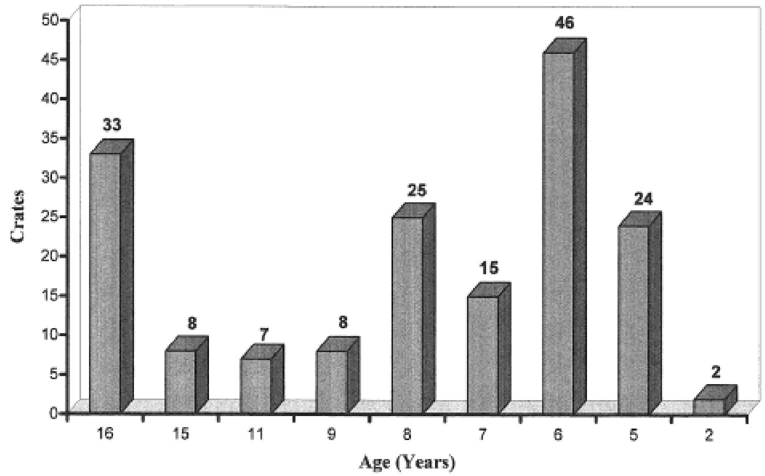

Figure 1 Age of post-used HDPE bottle crates.

ing on the processing stability and mechanical performance of restabilized, post-used, HDPE material from bottle crates was investigated. For restabilization Recyclossorb 550 together with Tinuvin 326 were used.[19] In the present paper the same restabilization recipe is followed and the light stability of the same bottle crate material recycled through the remelting-restabilization technique is studied. Specimens were kept for 8000 h in a Weather-O-Meter and during this accelerated exposure tensile impact tests were carried out for both restabilized and nonrestabilized grades to estimate the light effect on the mechanical performance of the recycled material studied. Furthermore, surface microphotographs were obtained to monitor any effect on the surface of the final recycled product. A repigmentation step was also included to study the influence of new pigments on the light performance of the recycled material. In this case, the repigmented grades were also studied by colorimetric determinations of the color difference (ΔE) during the artificial weathering exposure. The results show that the restabilization improves very significantly the light stability of the postconsumer crate material, ensuring its re-use in the original application, i.e., closed loop recycling becomes feasible.

EXPERIMENTAL

Materials

Post-Used Material

The material examined was: granules from post-used, yellow Heineken HDPE bottle crates. In Hellenic Brewery SA the oldest yellow Heineken crates, stored in the waste warehouse, were randomly collected. The crates were washed and then supplied to Mornos SA (crate producer) for drying. Finally, the crates were granulated and stored.

Figure 1 presents the age of all crates collected for this study, and they were determined using manufacture's coding in the bottom of each crate. The average age was about 9 years.

Analysis of the homogenized crate material resulted only in small quantity of residual active stabilizers as follows: phenolic antioxidants, approximately 200 ppm; phosphite antioxidants, traces; benzotriazole type UV absorbers, approximatley 300 ppm; polymeric Hindered Amine Light Stabilizers (HALS), approximately 500 ppm.

The analysis of residual stabilizers was carried out by dissolving the polymer in boiling toluene, reprecipitation of the polymer in methanol, filtration, and then analysis of the solution by HPLC (antioxidants, phosphites, UV absorber) respectively by thin layer chromatography (TLC) (polymeric HALS) using an internal calibration.[21]

Stabilizers

The restabilization system used was provided from Ciba Specialty Chemicals Ltd., with the intention, as mentioned already, to reuse the material again in the form of bottle crates. In addition processing stabilizers a sufficient content of light stabilizers was considered to be a typical prerequisite for such a use.

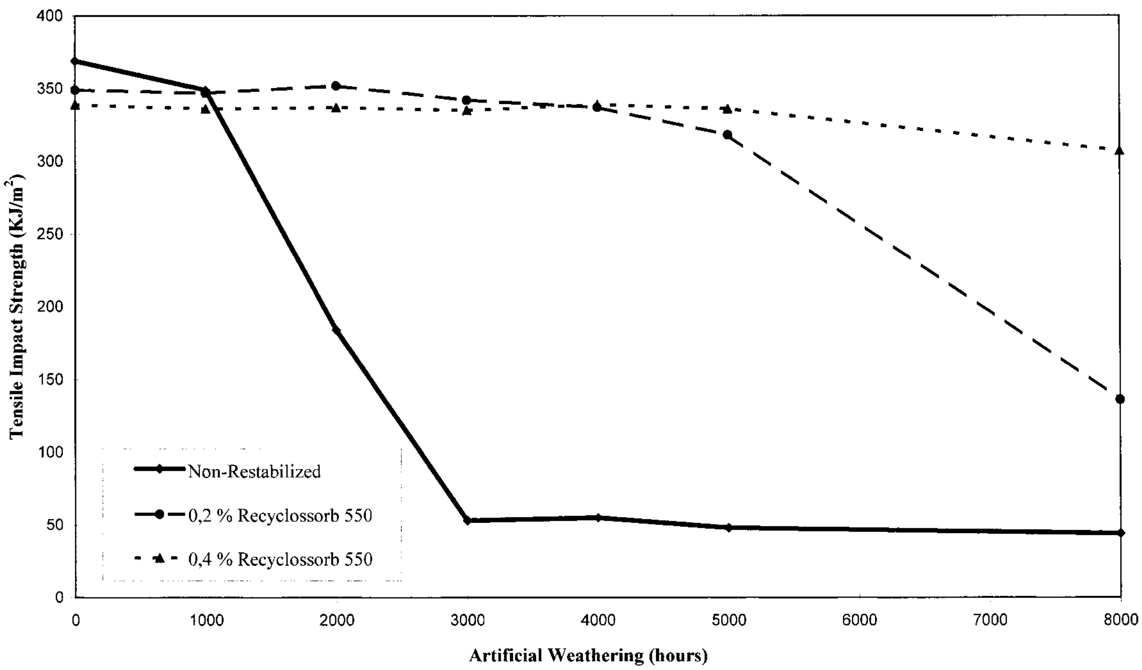

Figure 2 HDPE crates, nonrepigmented material: Effect of artificial weathering on the tensile impact test.

Pigments

For repigmentation, two different pigments, either a blue cooper-phthalocyanine-based or a red-organic-based, were used in the form of masterbatch.

Specimens Preparation

A Werner & Pfeiderer ZSK 25 twin-screw extruder and an Arburg 221-75-350 injection molding machine were used for preparation of speci-

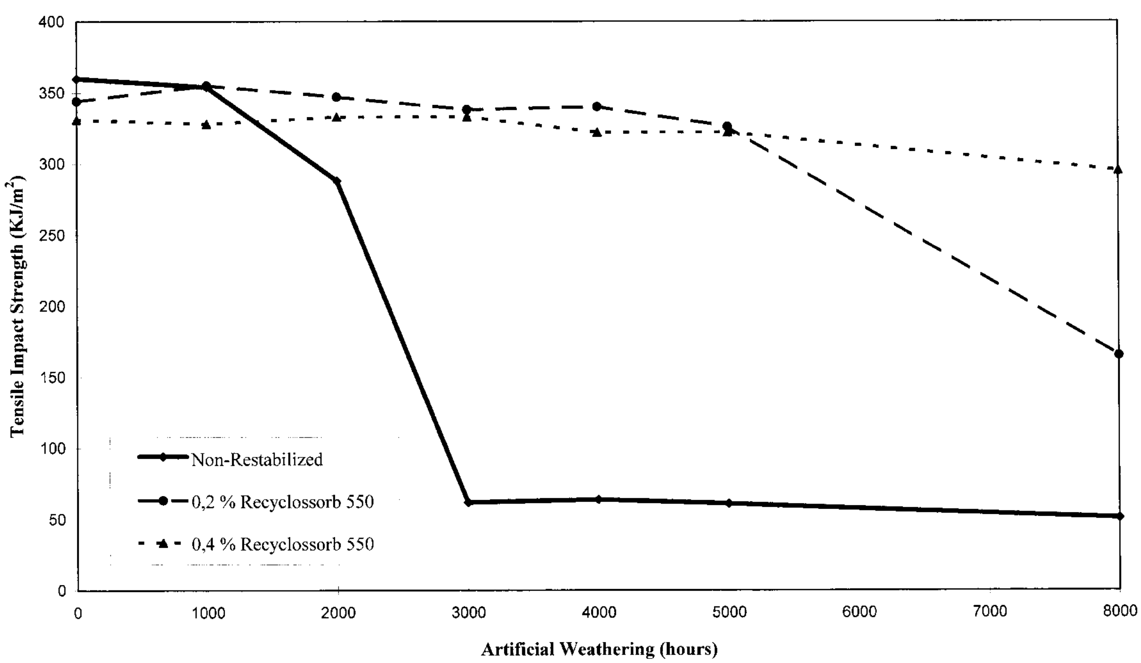

Figure 3 HDPE crates, green material: Effect of artificial weathering on the tensile impact test.

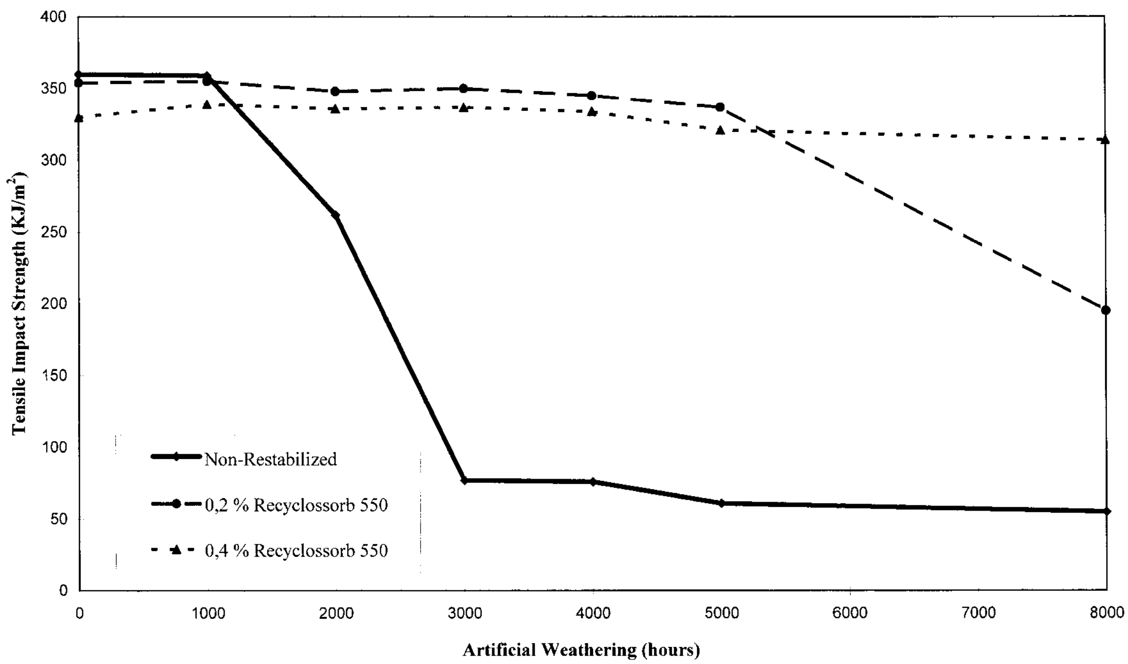

Figure 4 HDPE crates, orange material: Effect of artificial weathering on the tensile impact test.

mens. The experimental parameters of the twin-screw extruder were 100 rpm rotation speed and operation temperature at 250°C, whereas in the injection molding machine temperature and pressure were kept at the levels of 245°C and 50 bar, respectively. Passing through the twin-screw extruder ensures complete homogenization of the material. Specimens were prepared for both repigmented and nonrepigmented material and in three different qualities: (1) nonrestabilized specimens, (2) restabilized with 0.2% w/w Recyclossorb 550; and (3) restabilized with 0.4% Recyclossorb 550.

As mentioned already, a repigmentation stage has been included to determine the effect of new pigments on the light stability of the recycled crate material during artificial weathering. Because the original crate material was yellow colored, the blue pigment resulted in green coloring, whereas the red pigment resulted in orange.

Artificial Weathering

An Atlas Ci 65 A Weather-O-Meter was used for evaluating the light stability of the recycled crate material under accelerated conditions, according to ISO 4892 method. During this artificial weathering test a wet/dry cycle of 18 min/102 min was repeated. The test temperature was set at 63°C (Black Panel Temperature: 63°C), whereas the relative humidity at 60% (Relative humidity: 60%).

Tensile Impact Test

To correlate light stability with mechanical performance the tensile impact test was carried out for all different recipes after 0, 1000, 2000, 3000, 4000, 5000, and 8000 h of artificial weathering, according to the ISO 8256 or DIN 53 448 methods. A Zwick PSW 5101 tensile impact tester was used in standard laboratory atmosphere. The initial potential energy of the hammer was 25 J and the velocity at impact 3.4–4.1 m/s.

Microscopic Surface Examination

Surface microphotographs were obtained in a Zeiss microscope, equipped with a Polaroid camera, after 0, 4000, and 8000 h of artificial weathering for all grades. It should be noted that the study of the surface condition is very important, because only a relatively thin surface layer of the specimen is actually degraded from the light effect.[15]

Colorimetric Determinations

To evaluate the light effect on the repigmented materials, colorimetric determinations of the color difference (ΔE) were carried out after 0, 1000, 2000, 3000, 4000, 5000, and 8000 h of artificial weathering, according to DIN 6174 with the denomination ΔE (delta E) as per Hunter. A microprocessor controlled HUNTERLAB LABSCAN Spectro Colorimeter, type 5100 was used.

RESULTS AND DISCUSSION

Tensile Impact Test

Figure 2 illustrates the effect of artificial weathering on the tensile impact strength of the nonrepigmented recycled material. It is obvious that the tensile impact strength of the nonrestabilized grade starts decreasing dramatically after 1000 h of exposure, reflecting severe degradation on the polymer chain by photo-oxidation. On the other hand, the addition of the restabilization system used improves significantly the light stability of the recycled crate material, resulting in excellent retention of the tensile impact strength. In particular, the addition of 0.2% w/w Recyclossorb 550 ensures retention of the tensile impact strength at least for 5000 h, whereas the addition of 0.4% w/w of the restabilization system is necessary for keeping the retention above 90%, even after 8000 h exposure.

The effect of artificial weathering on the tensile impact strength for the green and orange repigmentation is presented in Figures 3 and 4, respectively. The repigmented grades present similar behavior as the nonrepigmented material. However, in the absence of stabilizer the addition of the new pigments seems to delay the dramatic deterioration of the tensile impact strength for a range of exposure between 1.000 to 2.000 h. This improvement is in line with previous findings where it was already shown that pigments alone prolong weatherability of HDPE to a certain extent.[22]

Microscopic Surface Examination

The microphotographs in Figure 5a–c present the evolution of the surface conditions for the nonrestabilized recycled material during the artificial weathering test. As can be seen, after 4000 h the surface suffers from crack formation mainly in the transverse direction of the specimen. In this case, the cracks are discontinuous and cover only a part of the specimen surface. Furthermore, bleaching and discoloration become visible. For longer exposure times the number and the size of the cracks further increase and after 8000 hours of artificial weathering the surface seems totally destroyed by continuous rifts (deep cracks), mainly in the transverse direction, accompanied by severe bleaching and discoloration.

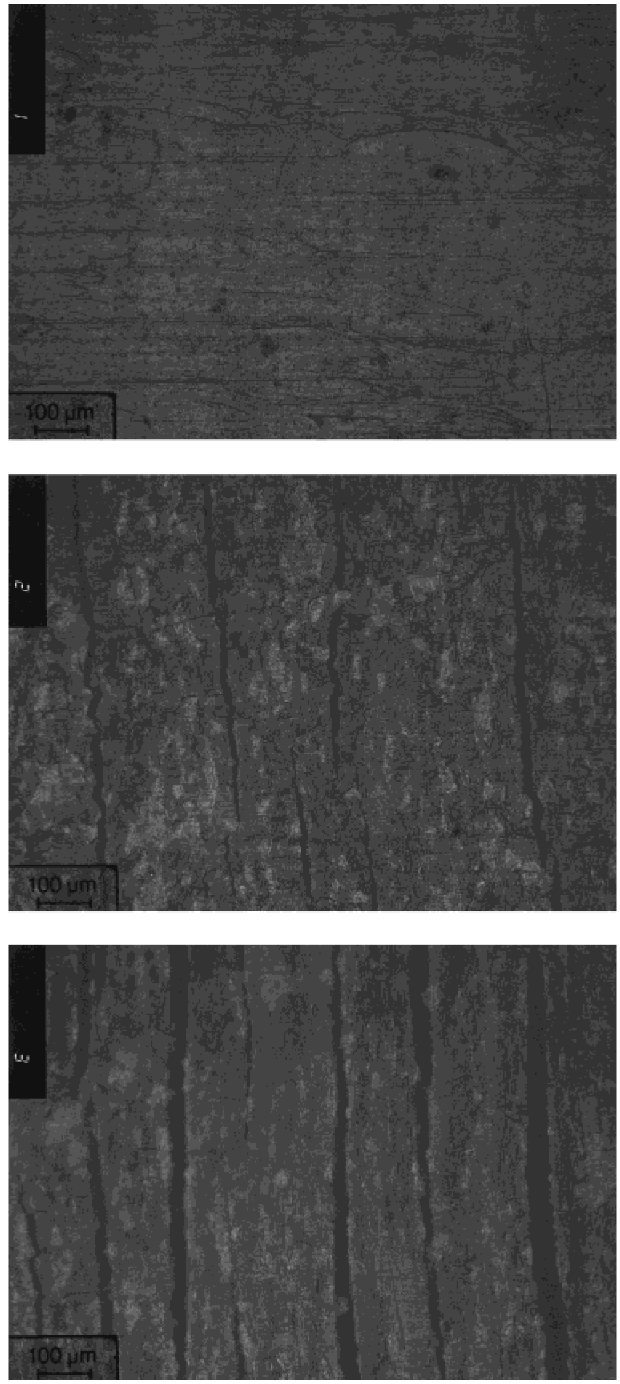

Figure 5 HDPE crates, nonrepigmented, nonrestabilized material: Effect of artificial weathering on the surface condition. (a) 0 h; (b) 4000 h; (c) 8000 h.

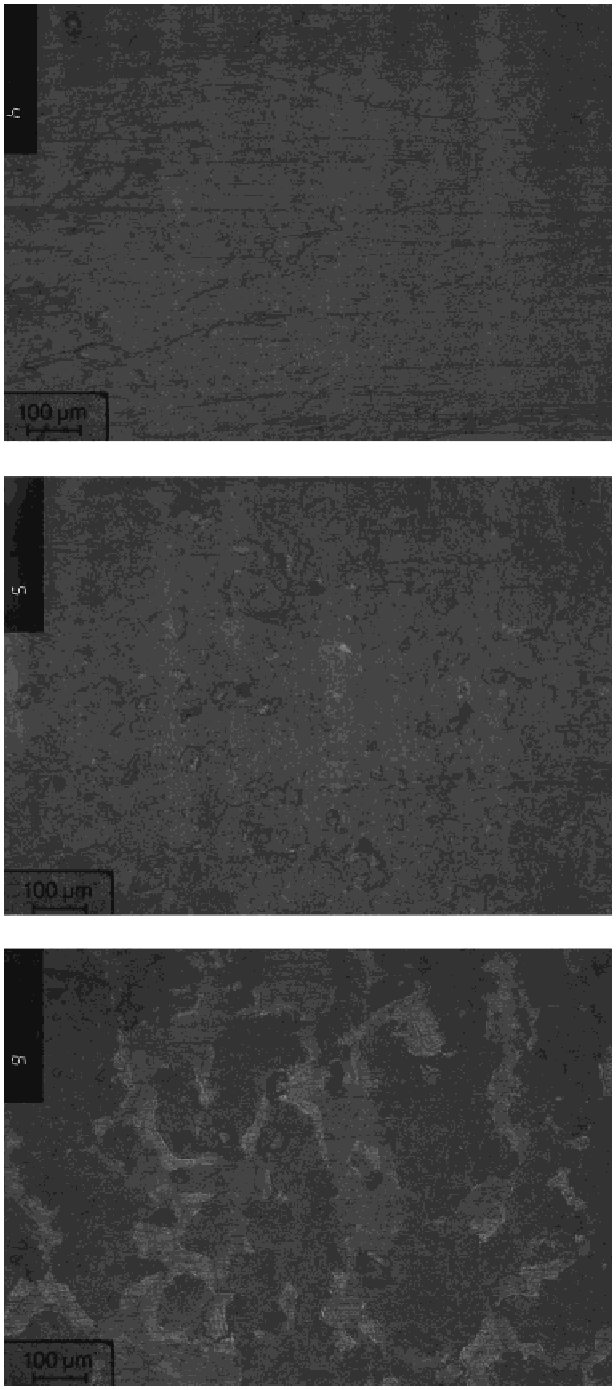

Figure 6 HDPE crates, nonrepigmented, restabilized material using 0.2% Recyclossorb 550: Effect of artificial weathering on the surface condition. (a) 0 h; (b) 4000 h; (c) 8000 h.

The microphotographs in Figures 6a–c and 7a–c present the surface conditions of restabilized material containing 0.2% w/w and 0.4% w/w of Recyclossorb 550, respectively. It is very impressive to realize that in both cases, the restabilizer increases the stability of the recycled old crate material so that the surface remains free from rifts and crack formation even after 8000

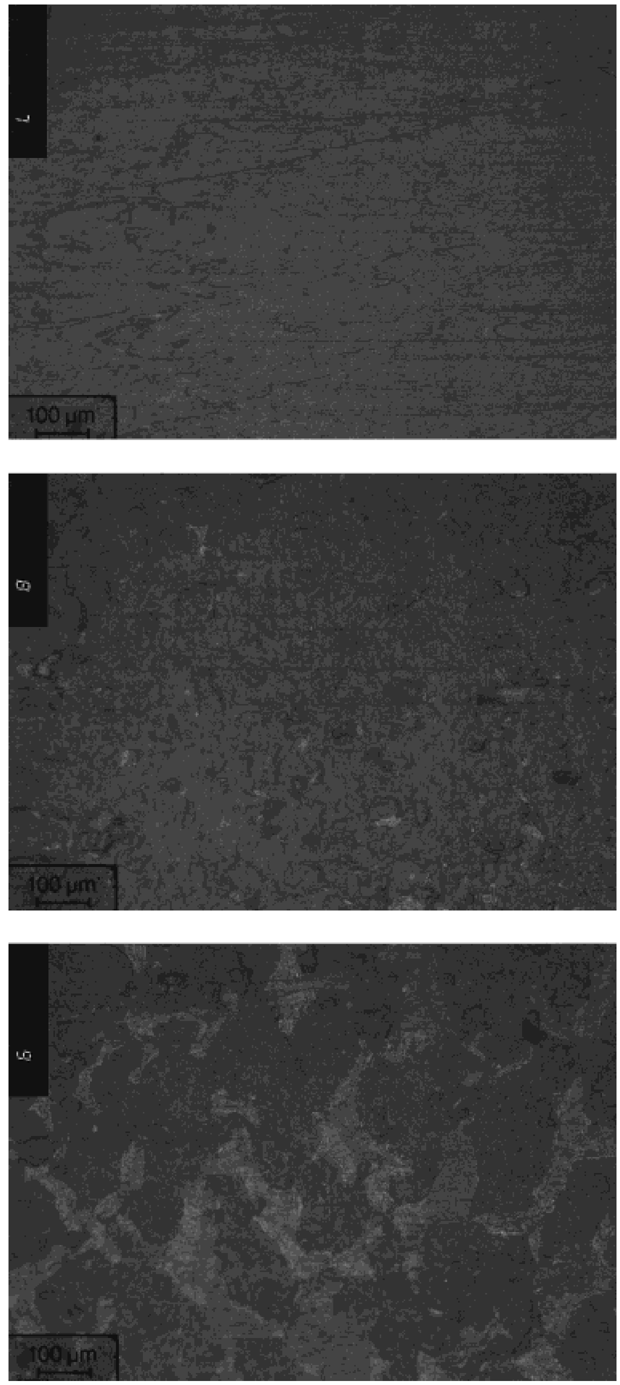

Figure 7 HDPE crates, nonrepigmented, restabilized material using 0.4% Recyclossorb 550: Effect of artificial weathering on the surface condition. (a) 0 h; (b) 4000 h; (c) 8000 h.

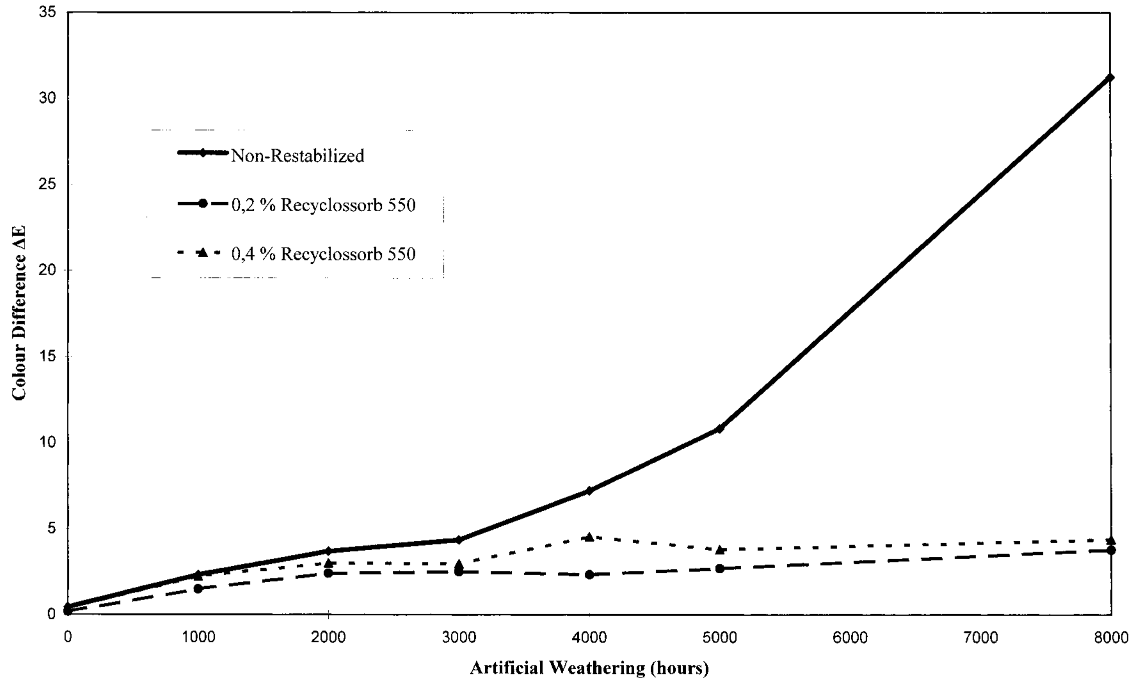

Figure 8 HDPE crates, green material: Effect of artificial weathering on the color difference (ΔE).

hours of exposure. It is worthwhile to add here that from literature[23] it is known that virgin HDPE is suitable for crates if artificial weathering of 6000–8000 h is survived with no or only minor loss of mechanical properties and surface aspects.

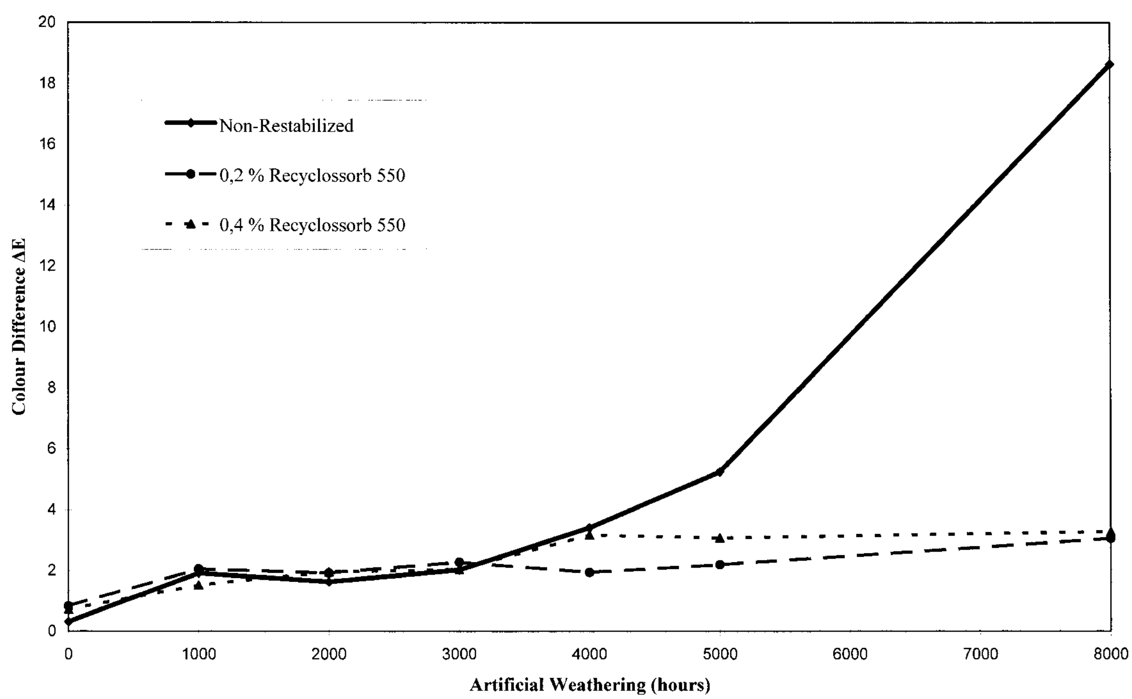

Figure 9 HDPE crates, orange material: Effect of artificial weathering on the color difference (ΔE).

Finally, it was found that the addition of the new pigments (green or orange) does not change the aforementioned view. Furthermore, in this case and for the nonrestabilized grades, the specimen surface appears even more damaged with deeper rifts than in the nonrepigmented, nonrestabilized material. However, the repigmented materials could be protected by restabilization as well as the nonrepigmented one.

Colorimetric Determinations

Figures 8 and 9 illustrate the effect of artificial weathering on the color difference (ΔE) for the green and orange repigmentation, respectively. Clearly, the ΔE values of the nonrestabilized grade deviate significantly after 3000 h of exposure reflecting severe discoloration on the repigmented samples. On the contrary, the addition of the restabilization system used improves significantly the color stability of the repigmented grades, resulting in excellent retention of the ΔE values, i.e., in negligible discoloration.

It is also worthwhile to mention that the aforementioned results are in line with the mechanical tests data (Figs. 2–4), i.e., discoloration can be used as indicator for degradation and loss in mechanical properties.

CONCLUSIONS

Artificial weathering was applied to study photooxidation effects on recycled, postconsumer, yellow pigmented, HDPE bottle crates. In the absence of restabilization the tensile impact strength of the material decreases dramatically only after 1000 h of exposure

The addition of the proposed restabilization system (Recyclossorb 550) improves the light stability, resulting in excellent retention of the tensile impact strength for at least up to 8000 h in artificial exposure. However, the restabilization level becomes critical for longer exposure times.

Restabilization effectively eliminates the crack formation on the surface of the recycled material and even significantly reduces bleaching and discoloration. On the other hand, colorimetric determinations are in harmony with the aforementioned data.

Consequently, exposure in artificial weathering for about 1 year proved that restabilization is mandatory for the light stability of the old crate material ensuring its reuse in the original application.

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