Closed-Loop Recycling of Postused PP-Filled Garden Chairs Using the Restabilization Technique. III. Influence of Artificial Weathering

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ABSTRACT: Artificial weathering was performed for 4000 h to evaluate the light stability of postused, $CaCO_3$-filled polypropylene material recycled from garden chairs. The old chair material was recycled by applying the remelting–restabilization technique while using different stabilization systems in selected concentrations. To study the role of restabilization in the material performance, the tensile impact strength was monitored during the artificial weathering exposure. The data were compared to microphotographs of the specimens' surfaces. The effect of light on the material was further studied through yellowness index (Y.I.) determinations. The results revealed that the appropriate restabilization of the postconsumer chair material is mandatory for improving its light stability, ensuring its reuse in the original application. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1311–1318, 2003

Key words: plastics; recycling; restabilization

INTRODUCTION

Most plastic materials are strongly susceptible to oxidative degradation when exposed to sunlight during outdoor use. The result could include discoloration, embrittlement, deterioration of the molecular weight, and loss of mechanical performance, limiting the quality of the plastic product as well as its lifespan. Of course, the degradation level of the polymeric material on exposure to ultraviolet radiation by the combined action of light and oxygen depends, to a great extent, on the material nature, on the polymer synthesis (catalysts, structural defects, impurities), on the previous processing steps, as well as on the environment of the final application.[1–5] It is well established that the degradation of polypropylene (PP) when exposed to sunlight is expanded through a free-radical mechanism, leading to backbone scission of intercrystalline tie molecules, restructure of the amorphous regions, chalking and crack formation in the surface zone, and an associated rapid decrease in residual elongation. In other words, the sunlight exposure of PP inflicts, in addition to visual changes, a loss of mechanical performance as well as a transition from ductile-to-brittle behavior.[4–7]

When dealing with postused plastics, derived from outdoor applications, the material quality is often already seriously degraded, since, during its previous processing step and service life, it was subjected to irreversible chemical reactions, caused mainly by physical aging and thermo- and photooxidation. In addition, these predamaged structures are much more sensitive to further deterioration than are the corresponding virgin materials, as they already contain groups that can enhance photooxidation. In that case, mechanical recycling of postused plastics in the original, outdoor application is difficult, unless appropriate protection is applied.[8–10]

Restabilization, the upgrading method of postconsumer plastic material by adding new amounts of suitable stabilizers for processing and long-term protection, can equalize or at least reduce the UV light effect to such an extent that the required long-term stability for the new application is generated. As a result, the durability and the value of the recycled end product is increased.[1,8–15] However, it should be mentioned that the restabilization recipe plays a very crucial role for achieving the targeted results. This recipe is highly dependent on the polymeric matrix type, the polymer morphology and structure, as well as the type of the intended application. For example, the restabilization recipe is of great importance when dealing with plastics containing inorganic fillers, where it seems not quite enough to simply maintain the physical properties by the addition of optimized stabilizers.[16–19]

Inorganic fillers are commonly added to commercial thermoplastics to reduce cost, as well as to modify

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favorably properties such as stiffness. However, the presence of an inorganic filler affects critically the morphology and the structure of a semicrystalline polymer, resulting in modifications of its mechanical behavior, its physical characteristics, as well as its resistance against thermal and photooxidation.[3,20] For example, by absorbing and/or screening light energy, they can exhibit a protective effect or, alternatively, they may photoactivate and sensitize the photochemical breakdown of the polymer.[20] In addition, the polar groups on the filler surface adsorb antioxidants and light stabilizers by interfering with hydroxy, ester, or amine groups of these stabilizers, thus reducing their protective function. It is the addition of a typical filler deactivator or filler modifier that can reduce the adsorption of the stabilizers and improve again the long-term stability of the recycled product.[20–22]

As far as closed-loop recycling possibilities are considered, the light stability of the recycled material should be carefully studied after restabilization. Weather-O-Meter tests and outdoor aging are applicable for the assessment of the resistance against light.[11] In this case, the criteria considered include visual inspection and assessment together with mechanical tests. Particularly, natural or outdoor weathering can take years before it becomes possible to collect useful results. Thus, an increasing need has arisen for reliable predictions of the outdoor lifetime through accelerated or artificial weathering tests.[7] The most important feature of these tests is that they can accelerate photodegradation of the studied material by achieving continuous exposure to light at high-energy wavelengths, elevated temperatures, and relative humidity values.[3] When dealing with polyolefins, good correlation has been found between natural weathering and xenon arc Weather-O-Meter artificial exposure.[7]

In previous parts of our study, carried out jointly at NTUA and Ciba Spezialitätenchemie Lampertheim GmbH, different stabilization systems in selected concentrations were employed to investigate the optimum restabilization recipe for eliminating degradation effects during reprocessing and heat aging of postused, $CaCO_3$-filled PP material from garden chairs.[18,19] In this article, the same stabilization recipes were followed and the light stability of the same chair material was studied. Specimens of the recycled chair material were stored at 63°C (black panel temperature) for 4000 h in a Weather-O-Meter, and during this accelerated exposure, tensile impact tests were carried out for both restabilized and nonrestabilized grades to evaluate the mechanical performance of the recycled material. The influence of light was further studied through yellowness index (Y.I.) determinations. Additionally, for selected compositions, surface microphotographs were obtained to investigate any effects on the surface of the final recycled product.

EXPERIMENTAL

Starting material

The material examined was granules of postused, white pigmented, garden chairs manufactured from filled PP. The old chair material was randomly collected from a local landfill in Greece. The age of the postused chairs collected was estimated to be between 3 and 5 years. The chairs were carefully washed, dried, and then shredded and stored. Analysis of the homogenized chair material showed that it contained 15% $CaCO_3$ (determined by ASS), on average, while the basic pigment was TiO_2.

Analysis of residual stabilizer content, carried out using the HPLC technique, resulted only in a small quantity of active stabilizers in the range of

- Approximately 350 ppm phenolic-type primary antioxidants;
- No active phosphate-based secondary antioxidants;
- No active epoxide as a filler deactivator;
- No active UV absorbers or hindered amine (HALS) light stabilizers.

Restabilization systems

Three different stabilizer systems from Ciba Specialty Chemicals Ltd. (Lampertheim, Germany) were employed in selected concentrations to develop the optimum restabilization recipe for eliminating degradation effects during artificial weathering exposure. In addition to the processing stabilizers, a sufficient content of light stabilizers was considered to be a typical prerequisite to reuse the material again in the form of garden chairs:

- *Recyclostab 451®:* Stabilization system based on different types of antioxidants and costabilizers specifically developed to offer processing stability and long-term thermal protection for recycled plastics, especially for PP and polyolefin blends.
- *Recyclossorb 550®:* Stabilization system specifically developed for light stabilization of recycled plastics, but also it provides basic heat stability to polyolefin recyclates. It is a mixture of antioxidants, costabilizers, and light stabilizers.
- *Recycloblend 660®:* Stabilization system specifically developed for polyolefins against the negative influence of impurities, such as paint or ink residues during processing and application. Furthermore, it acts as a deactivator for compounds such as carbon black and fillers. It consists of antioxi-

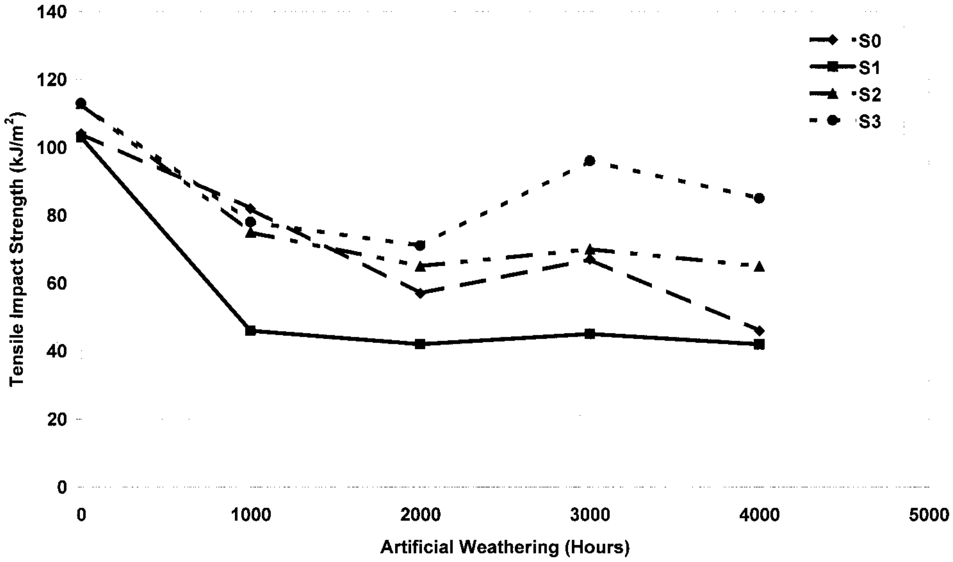


Figure 1 Filled PP chair recyclate reprocessed at 260°C: Effect of artificial weathering on tensile impact strength—I.

dants, coadditives, and selected oxirane compounds as reactive agents in a specific ratio.

Reprocessing and specimen preparation

A Werner & Pfeiderer ZSK 25 twin-screw extruder was used for reprocessing the old chair material, while an Arburg 221-75-350 injection-molding machine was employed for the preparation of the specimens to be exposed to artificial weathering. Using the twin-screw extruder, a single reprocessing cycle was performed, ensuring complete homogenization of the additives with the chair material.

The experimental parameters of the twin-screw extruder were a 100-rpm rotation speed and an operation temperature at 260 and 280°C, respectively. In the injection-molding machine, the temperature was kept at 250°C, while the injection pressure was set at the level of 50 bars.

Tests specimens were prepared in the following 11 compositions:

(a)**S0**: Original waste (PP chairs) material, injection-molded without a previous reprocessing step.

Reprocessed at 260°C:

(b) **S1** :Nonrestabilized material, reprocessed at 260°C.

(c) **S2** :Restabilized material using 0.2% w/w Recyclossorb 550® and 0.2% w/w Recyclostab 451®, reprocessed at 260°C.

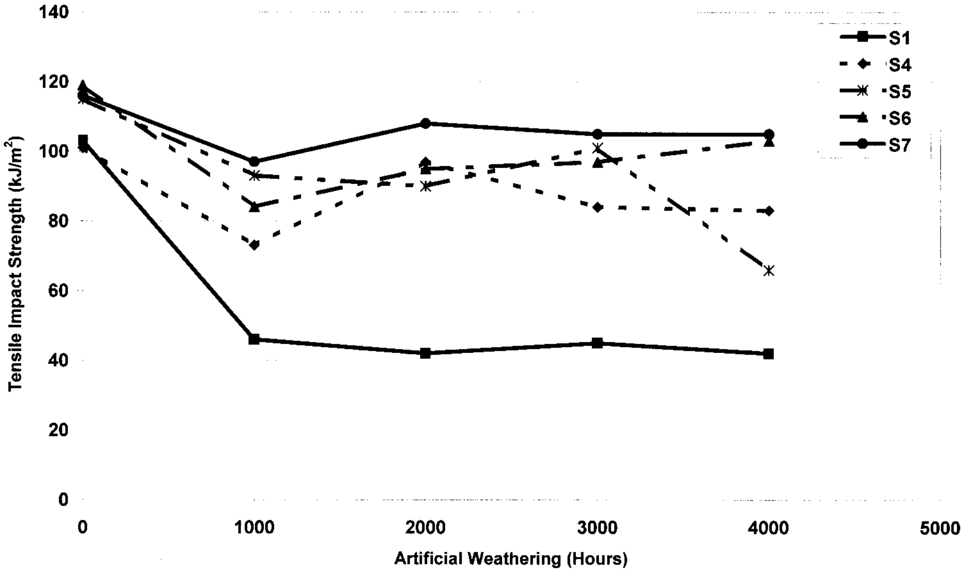


Figure 2 Filled PP chair recyclate reprocessed at 260°C: Effect of artificial weathering on tensile impact strength—II.

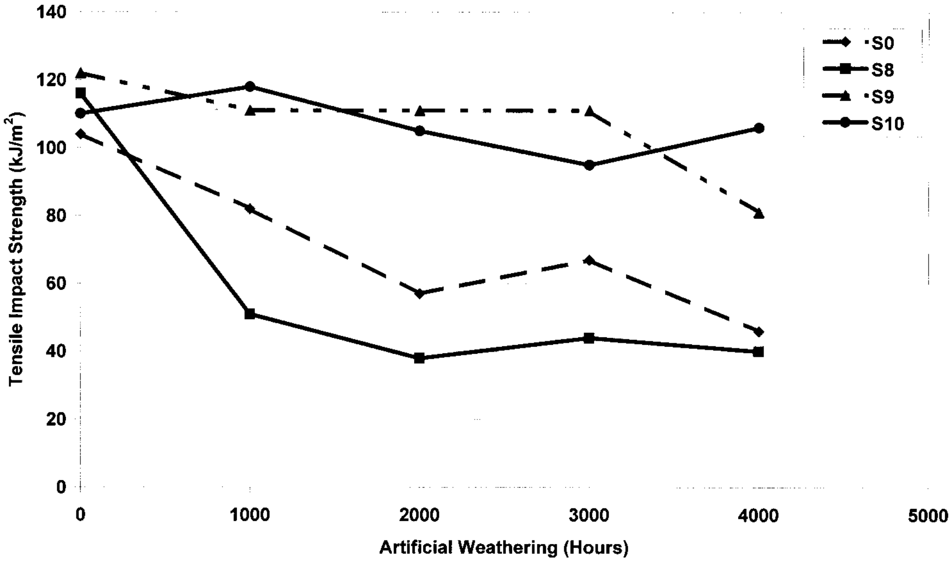


Figure 3 Filled PP chair recyclate reprocessed at 280°C: Effect of artificial weathering on tensile impact strength.

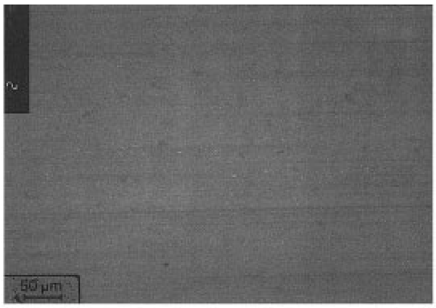
(d) **S3** :Restabilized material using 0.4% w/w Recyclossorb 550® and 0.4% w/w Recyclostab 451®, reprocessed at 260°C.
(e) **S4** :Restabilized material using 0.2% w/w Recyclossorb 550® and 0.2% w/w Recycloblend 660®, reprocessed at 260°C.
(f) **S5** :Restabilized material using 0.2% w/w Recyclossorb 550® and 0.5% w/w Recycloblend 660®, reprocessed at 260°C.
(g) **S6** :Restabilized material using 0.4% w/w Recyclossorb 550® and 0.5% w/w Recycloblend 660®, reprocessed at 260°C.
(h) **S7** :Restabilized material using 0.4% w/w Recyclossorb 550® and 1% w/w Recycloblend 660®, reprocessed at 260°C.

Reprocessed at 280°C:

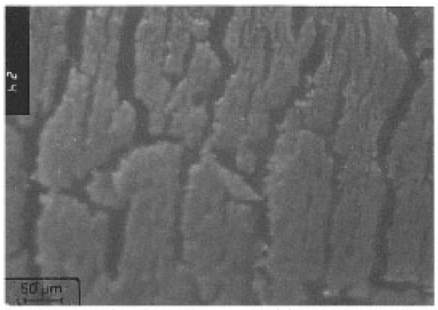
(a) **S8** :Nonrestabilized material, reprocessed at 280°C.
(b) **S9** :Restabilized material using 0.2% w/w Recyclossorb 550® and 0.5% w/w Recycloblend 660®, reprocessed at 280°C.
(c) **S10** :Restabilized material using 0.4% w/w Recyclossorb 550® and 1% w/w Recycloblend 660®, reprocessed at 280°C.

Artificial weathering

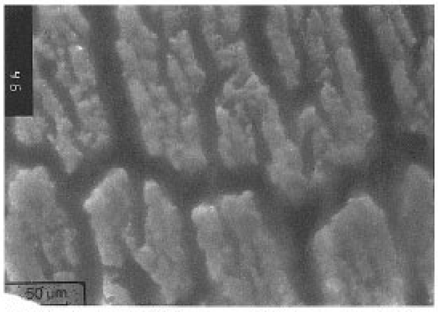
An Atlas Ci 65 A Weather-O-Meter was used for evaluating the light stability of the recycled chair material under accelerated conditions, according to the ISO 4892 method. Specimens of all the different grades prepared were subjected for 4000 h to artificial weathering at a standard wet/dry cycle of 18/102 min. The



4a. Non-restabilized material (S1) **0 hours of artificial weathering**

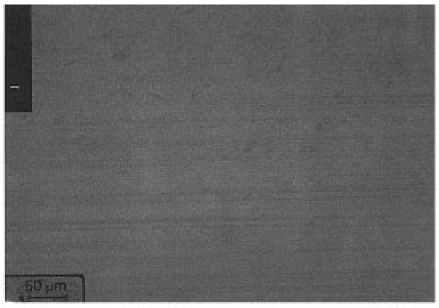


4b. Non-restabilized material (S1) **2000 hours of artificial weathering**

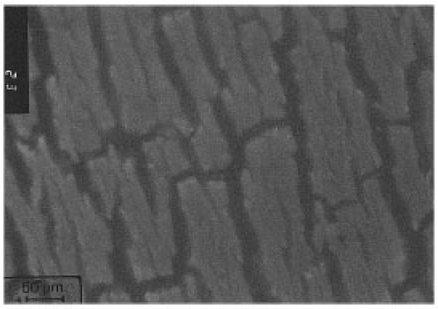


4c. Non-restabilized material (S1) **4000 hours of artificial weathering**

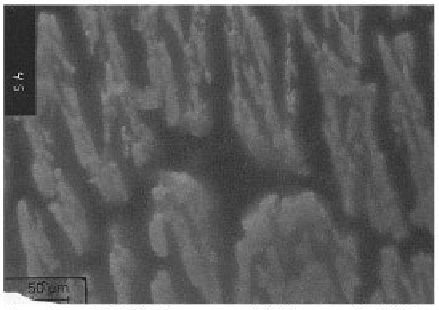
Figure 4 Filled PP chair, nonrestabilized material (*S1*): Effect of artificial weathering on the surface condition.



5a. **Original waste material (S0)** **0 hours of artificial weathering**



5b. **Original waste material (S0)** **2000 hours of artificial weathering**



5c. **Original waste material (S0)** **4000 hours of artificial weathering**

Figure 5 Filled PP chair, original waste material (*S0*): Effect of artificial weathering on the surface condition.

test temperature was set at 63°C (black panel temperature), and the relative humidity, at 60%.

Tensile impact test

To correlate light stability with mechanical performance, a tensile impact test was carried out for all different recipes after 0, 1000, 2000, 3000, and 4000 h of artificial weathering, according to the ISO 8256 or DIN 53 448 methods. A Zwick PSW 5101 tensile impact tester was used in a standard laboratory atmosphere. The initial potential energy of the hammer was 25 J and the velocity at impact 3.5–4 m/s.

Microscopic surface examination

Surface microphotographs were obtained in a Zeiss microscope, equipped with a Polaroid camera, after 0, 2000, and 4000 h of artificial weathering for all grades. The study of the surface condition is very important, since, with a polymer such as PP, only a relatively thin surface layer of the specimen is actually degraded by photooxidation.[15]

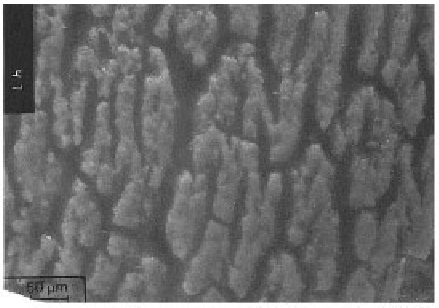
Y.I. determinations

To assess further the light stability of all different grades of the recycled chair material, subjected to artificial weathering conditions, Y.I. determinations were carried out after 0, 1000, 2000, 3000, and 4000 h of exposure, according to ASTM D 1925-70. In all the determinations employed, a Minolta Spectro-Photometer, type CM 3600 D, was used.

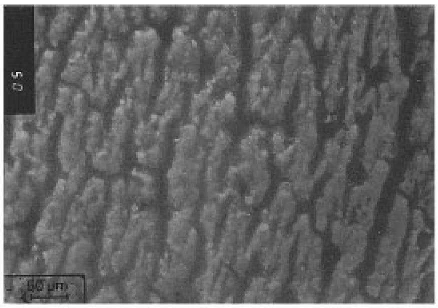
RESULTS AND DISCUSSION

Tensile impact test

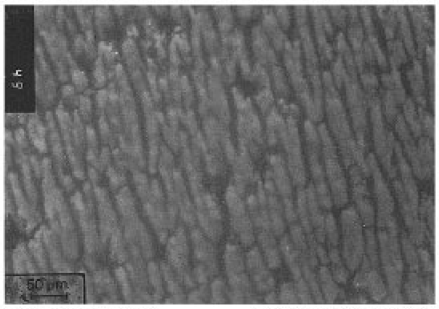
Figures 1 and 2 illustrate the effect of artificial weathering on the tensile impact strength of the recycled chair material, for all the different grades reprocessed



6a. **Restabilized material (S2)** **4000 hours of artificial weathering**



6b. **Restabilized material (S4)** **4000 hours of artificial weathering**



6c. **Restabilized material (S7)** **4000 hours of artificial weathering**

Figure 6 Filled PP chair, restabilized grades (*S2*, *S4*, *S7*): Effect of artificial weathering on the surface condition.

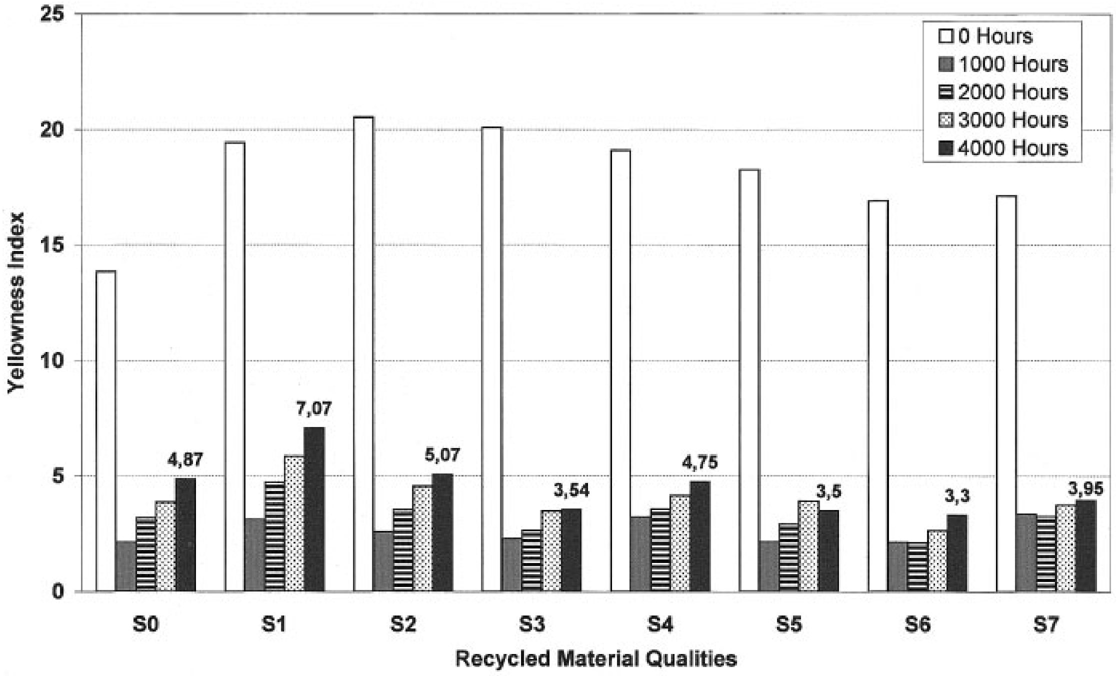


Figure 7 Filled PP chair recyclate reprocessed at 260°C: Effect of artificial weathering on Y.I.

at 260°C. As can be seen, the tensile impact strength of all different grades employed starts decreasing after the first 1000 h in the Weather-O-Meter, but in the case of the nonrestabilized (*S1*) material, the recorded decrease is very intensive, reflecting severe degradation on the polymer chain mainly caused by photooxidation. It is important to mention also that after completing this short exposure period the tensile impact strength of the nonrestabilized grade is below 50% of the original value, which means that the nonrestabilized material was proved to be unsuitable for reuse in the original application. On the other hand, the samples prepared from the original waste material (*S0*) present higher resistance against light effects, especially at the early stages of the artificial exposure. Based on this observation, it is verified that the induced degradation of the nonrestabilized material during reprocessing dramatically affects the light stability of the old chair material, limiting significantly its mechanical performance unless appropriate protection is applied.[18]

Turning now to the restabilized grades, the results prove that, in all cases studied, the addition of stabilizing agents delay the dramatic deterioration of the tensile impact strength of the recycled PP-filled chair material. However, the restabilization recipe plays a very important role. As can be seen in Figure 1, the addition of the restabilization system Recyclostab 451®, together with the system Recyclossorb 550® (*S2* and *S3*), offers only limited protection for the recycled chair material against the influence of light, resulting in poor retention of the original tensile impact strength. On the contrary, the synergistic action of Recyclossorb 550® with the especially designed system Recycloblend 660®, which acts also as filler deactivator, definitely improves the light stability of the material. Figure 2 shows that the addition of Recycloblend 660®, (*S4–S7*) to the recycled chair material leads to higher tensile impact strength retention. However, the restabilization level is still crucial. It should be noted that only by the addition of Recycloblend 660®, at the higher concentration level of 1% w/w (*S7*) can the light stability of the recycled material be upgraded significantly, resulting in excellent retention of the tensile impact strength, even after 4000 h of artificial weathering.

The aforementioned view was also recorded in the samples reprocessed at 280°C, plotted in Figure 3. As can be clearly seen, the addition of Recyclossorb 550® together with the filler deactivator Recycloblend 660®, at the concentration of 1% w/w (*S10*), is necessary for keeping the tensile impact strength of the recycled chair material above 90% of the original value, even after 4000 h of artificial weathering.

Microscopic surface examination

The microphotographs in Figure 4 (a–c) present the evolution of the surface condition for the nonrestabilized recycled material (*S1*), reprocessed at 260°C, during artificial weathering exposure. As can be seen, even after 2000 h, the surface suffers from crack formation, mainly at the longitudinal direction of the specimen. The cracks are almost continuously cover-

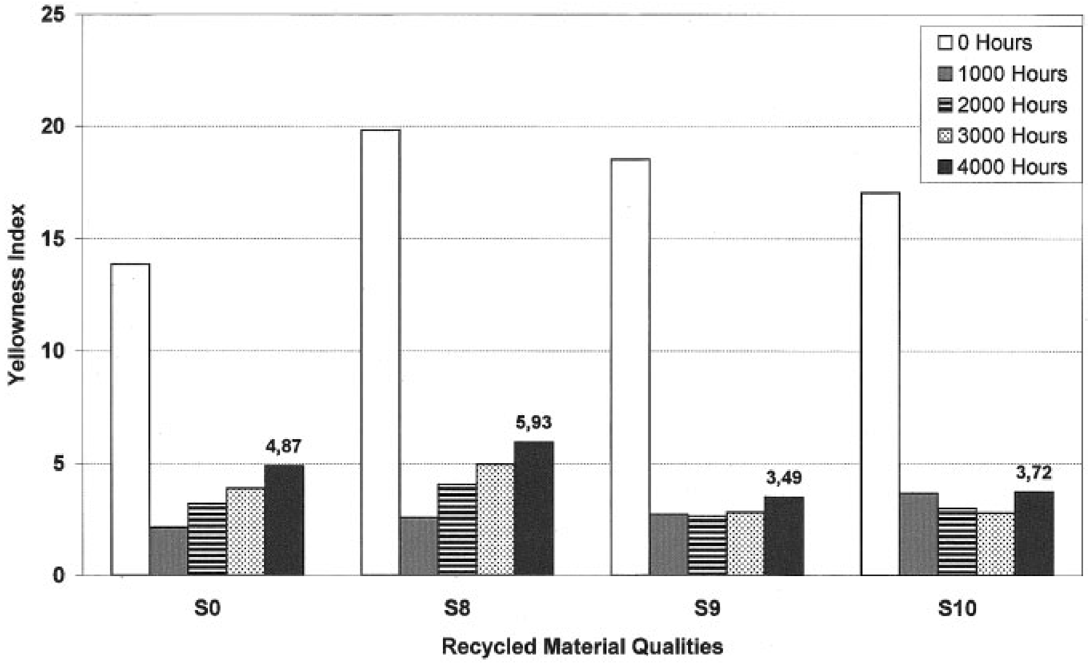


Figure 8 Filled PP chair recyclate reprocessed at 280°C: Effect of artificial weathering on Y.I.

ing the complete surface area. For longer exposure times, the deterioration of the surface accelerates, and after 4000 h, the surface specimen seems totally destroyed with continuous, wide, and deep cracks (rifts) in both specimen directions. It is obvious that the induced photooxidation during the artificial weathering test irreparably degraded the surface of the nonrestabilized material, limiting its performance and value. The same view can be also observed in the microphotographs of the Figure 5(a–c), where the evolution of the surface condition for the original waste material (*S0*) is presented.

On the other hand, by studying the surface microphotographs of all restabilized specimens, reprocessed at 260°C, it is shown that the addition of new stabilization agents to the old chair material can eliminate or at least reduce the photooxidative degradation mechanism induced during artificial weathering. The microphotographs in Figure 6(a–c) present the surface condition of three different restabilized materials after 4000 h in the Weather-o-Meter. Figure 6(a) presents the surface of the recycled material, containing 0.2% w/w of Recyclossorb 550® together with 0.2% w/w of Recyclostab 451® (*S2*). Figure 6(b) presents the surface of the recycled material, containing 0.2% w/w of Recyclossorb 550® together with 0.2% w/w of Recycloblend 660® (*S4*), and, finally, the surface condition of the material containing 0.2% w/w of Recyclossorb 550® together with 1% w/w of Recycloblend 660® (*S7*) is presented in Figure 6(c). As can be seen in all cases, after 4000 h of artificial weathering, the crack formation on the specimens' surfaces remains limited comparably with the surface condition of the nonrestabilized material. However, by comparing microphotographs 6(a) and 6(b), it is clear that the type of restabilization is important. As can be seen, the replacement of Recyclostab 451® by the filler deactivator Recycloblend 660®, at the level of 0.2% w/w, improves the light stability of the old chair material, limiting the deterioration (crack formation) of the surface. On the other hand, comparison between microphotographs 6(b) and 6(c) reveals that the restabilization level is also very crucial. The addition of Recycloblend 660®, in the higher concentration level of 1% w/w, upgrades the light stability of the recycled material in a way that the crack formation on the specimen surface seems to be very remarkably reduced. In other words, the addition of the filler deactivator at the high concentration level is mandatory for improving the resistance of the recycled chair material against light attack, which is an essential prerequisite for the reuse in the original application. Finally, it should be mentioned that the aforementioned view was also observed in the recycled grades, reprocessed at 280°C.

Y.I. determinations

Figure 7 illustrates the effect of artificial weathering on the Y.I. of all different grades reprocessed at 260°C. The YI of the samples before artificial weathering reflects a light ebony-colored aspect. As can be seen in all recipes examined, an impressive decrease of the Y.I. values is recorded after the first 1000 exposure hours. This trend is common for both restabilized and nonrestabilized grades and it could be possibly chalking, that is, the degradation of the surface to low molecular weight material. Simultaneously, a loss of surface gloss is observed.

However, as can be seen in Figure 7, for longer exposure times, the Y.I. values of all the different recipes employed start increasing gradually until the end of the artificial weathering test (4000 h). Such a trend could be attributed possibly to yellow discoloration caused by the photooxidation effect in addition to the chalking. It is important to note that the nonrestabilized material (*S1*) presents a higher Y.I. value (7.1) after the end of the artificial weathering test, reflecting the higher discoloration level. On the other hand, the addition of the stabilization agents seem to delay the increase of the Y.I. The same view was recorded in the case of the recycled grades, reprocessed at 280°C and presented in Figure 8.

CONCLUSIONS

Artificial weathering was applied to study photooxidation effects on recycled $CaCO_3$-filled PP material from postused garden chairs. Without restabilization, the tensile impact strength of the material decreases dramatically even after 1000 h of exposure, indicating complete loss of mechanical properties. The addition of the appropriate restabilization recipe improves the light stability, resulting in high retention levels of the tensile impact strength for at least up to 4000 h of artificial exposure.

Additionally, the restabilization effectively reduces the crack formation on the surface of the recycled material. However, the restabilization type and level do become critical. On the other hand, Y.I. determinations suggest that restabilization of recycled material could not completely avoid chalking but delays its yellow discoloration.

The presence of the filler in the polymer matrix affects negatively the light stability of the recycled material, but as demonstrated, this effect can be considerably controlled by the addition of a filler deactivator. The addition of this compound proved to be mandatory since it could effectively block the consumption of the light stabilizers into the filler's porosity, prolonging weatherability of the recycled material. The latter is an essential prerequisite for its reuse in the original application.

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