Mechanical Recycling of Postused High-Density Polyethylene Crates Using the Restabilization Technique. I. Influence of Reprocessing

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ABSTRACT: A remelting–restabilization technique was applied for the recycling of postused, yellow-pigmented high-density polyethylene (HDPE) bottle crates. Multiple extrusion cycles procedure, at different reprocessing temperatures, was performed for monitoring the processing stability of the restabilized and nonrestabilized material as reference. In addition, mechanical properties measurements were carried out, to study further the effect of restabilization on the performance of the recycled material. Finally, repigmentation was used to investigate the role of new pigments on the final recycled product. The results illustrate that restabilization of postused crates leads to careful reprocessing without severe degradation, which is an essential prerequisite for reuse in the original application. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1775–1785, 1999

Key words: plastics recycling; mechanical recycling; restabilization, HDPE bottle crates

INTRODUCTION

Approaches to plastics recycling mainly include three recycling options: (1) mechanical or material recycling; for example, direct reuse without polymer modification; (2) chemical recycling; for example, depolymerization and reuse of monomers; and (3) energy recovery; for example, use of calorific value of polymer wastes.[1–4] In recent years, it has been accepted that material recycling is the most efficient and reliable method of dealing with plastic waste. Among the material recycling technologies that have already been developed, the remelting technique; that is, reprocessing in the melt phase, remains the most effec-

tive, popular, economical and easily applicable method.[5–9] Nevertheless, this technology often leads to degraded products of inferior value, because plastics, as organic materials, are subjected to undesirable chemical reactions during their previous processing steps and service life, mainly caused by oxidation and photo-oxidation. These chemical reactions lead to irreversible changes in the polymer structure, affecting the physical properties and the quality of the polymer.[4–6,10–14] On one hand, during their service life, plastics suffer from natural aging from the influence of temperature, air, light, and weathering, leading to degradation of their visual and mechanical properties. On the other hand, during processing, plastics undergo preliminary molecular damage, such as chain scission, crosslinking, or formation of double bonds.[15]

In particular, extrusion is one of the most damaging procedures to which a polymer could be

Figure 1 HDPE crates, nonrepigmented material: effect of multiple extrusion on MFR at 220°C.

subjected. The shear forces together with the high processing temperatures lead to mechanical scission of the polymer chain, which produces highly reactive macroradicals at the end of the chain. In the presence of small amounts of oxygen, these radicals cannot recombine, but form peroxyl radicals and hydroperoxides. These chemical reactions lead to molecular weight degradation, and the plastic becomes unsuitable for its original use.[4,10,12,14,15]

In addition, as a rule, polymers are stabilized only for their first life, but this original stabilization is generally insufficient for reprocessing and second life application.[8,9,11,16] Therefore, quality improvement of the recycled plastics becomes the key issue. To achieve upgrading of recycled plas-

tics, not only sophisticated cleaning and separation is needed, but also material properties must be optimized. There are different ways to improve the quality of the recyclates, mainly by mixing with virgin material, or by restabilization.[11,17]

Restabilization, which means addition of processing, thermal, and light stabilizers in the postused polymer, aims to minimize degradation effects during the reprocessing stage and reuse. In other words, the objective is, depending upon the material, to avoid degradation of the polymer chain and side reactions, such as crosslinking, and to maintain the molecular weight, the rheological behavior, and the mechanical properties of the recyclate, as well.[7–13,16–19]

Figure 2 HDPE crates, nonrepigmented material: effect of multiple extrusion on MFR at 250°C.

Figure 3 HDPE crates, nonrepigmented material: effect of multiple extrusion on MFR at 280°C.

In the case of reprocessing high-density polyethylene (HDPE), the polymer suffers from degradation, which alters the chain length and branching, along the polymer structure. The thermal/oxidative and thermal/mechanical degradation of the polymer, lead to crosslinking or chain scission phenomena. Both events are competitive and occur simultaneously to varying degrees during processing of HDPE. Depending mainly, upon the catalyst type used, on processing conditions, and oxygen availability, any of the aforementioned mechanisms might prevail over the other.[20,21] In a Phillips-type HDPE, crosslinking mechanism seems to predominate over the chain scission, leading to a recombination of the polymer radicals and

to a final increase in the chain length or branching. On the other hand, a Ziegler-type HDPE mainly undergoes chain scission mechanism during processing, causing a molecular length reduction.[13,22,23] Both mechanisms interact on the molecular weight of the polymer, causing problems in the melt flow, in the mechanical strength, and the physical characteristics of the polyolefin.[22] In practice, however, more severe problems are encountered because of crosslinking effects, because the formation of very large insoluble molecules, so-called gels, leads to inhomogeneity of polymer melt and, consequently, to deficient end products.[20]

Recycling of HDPE is of primary interest, because it is one of the major components of munic-

Figure 4 HDPE crates, nonrepigmented material, nonrestabilized: MFR differences after successive reprocessing cycles.

Figure 5 HDPE crates, nonrepigmented material, containing 0.2% Recyclossorb: MFR differences after successive reprocessing cycles.

ipal solid waste plastic frame. In 1996 HDPE, constituted about 14.3% of the total plastics consumption in Western Europe (3.7 in 26.0 million tons). About 70% of the total HDPE consumption enters the waste streams in less than 2 years, because the HDPE homopolymers are commonly used for film, bottle, and container applications.[2] A further stream of HDPE consists of well-defined long-term applications, such as crates, containers, automotive, and electrical parts. The mechanical recycling of this easily collected scrap is mandatory. Therefore, careful restabilization could face up to the aforementioned degradation problems, providing high-quality recyclates for a second life, or, preferably, in the original application.

Bottle crates are an example of a very well-defined recyclate stream, where old material is collected by the bottlers. Today, old material is reused in new crates but only in small amounts added to virgin material. In the future 100% reuse is predicted.

There are some examples of quality improvement of HDPE products through restabilization. Previous studies from Ciba Specialty Chemicals Inc. show that successful recycling of HDPE end products can be effected by using restabilization; for example, in recycling HDPE bottle crates at different processing temperatures. The stabilizers used were processing stabilizers (Irganox 1010, Igrafos 168), based on hindered phenols or phosphites.[13,23] In another example, the use of light stabilizers, such as hindered amines or UV absorbers (HALS-1 and UVA-1), in addition to an antioxidant blend of hindered phenols and phos-

phites (Irganox B 215), results in quality improvement of HDPE crate material.[11,17]

Other studies showed that the addition of 0.1% w/w each of the two aforementioned components Irganox 1010 and Irgafos 168, permits maintaining melt flow value constant during multiple extrusions of a HDPE container material.[16] Research in Ciba Specialty Chemicals Inc. reveals that the restabilization of typical blue pigmented HDPE material from drums, with the addition of a new processing stabilizer (Recyclostab 411), especially developed for recycling, prevents degradation during processing.[19] Vink et al. showed that efficient light stabilization of degraded yellow-pigmented HDPE crates can be accomplished by the addition of a hindered amine type stabilizer (Tinuvin 770, product of Ciba Specialty Chemicals, Inc.), giving the opportunity for outdoor use of the recycled material.[24]

The aim of this article is to study in detail the upgrading possibilities of postused, yellow-pigmented HDPE bottle crates through the remelting–restabilization technique to prove closed-loop recycling possibilities. A new restabilization system is used, marketed under the trade name Recyclossorb 550 (product of Ciba Specialty Chemicals, Inc.), which is a combination of processing and light stabilizers, especially developed for recycling of polyolefins from/for outdoor applications. To evaluate the effect of the restabilization applied, the processing stability at different reprocessing temperatures and the mechanical performance of the recycled material are studied. Multiple extrusion cycles are performed to simulate the reprocessing effect on the melt flow, and

Figure 6 HDPE crates, nonrepigmented material, containing 0.4% Recyclossorb: MFR differences after successive reprocessing cycles.

tensile and tensile impact tests are carried out for estimating the performance of the recycled material. Finally, the effect of the addition of a new pigment on the final recycled product is evaluated by a repigmentation step. In a second part, the influence of artificial weathering is foreseen to be studied at a later stage.

EXPERIMENTAL

Materials

The material examined was: granules from postused, 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. The average age of the crates was almost 9 years. Analysis of the homogenized crate material shows only a small quantity of residual active stabilizers in the range of: approx. 200 ppm of phenolic antioxidants; traces of phosphites; approx. 300 ppm of benzotriazole-type UV absorbers; and approx. 500 ppm of polymeric HALS.

The restabilization systems used were products of Ciba Specialty Chemicals, Ltd. These systems were chosen with the aim to reuse the material again in the form of crates. In addition to processing stabilizers, a sufficient content of light stabilizers is believed to be essential. Besides hindered amine stabilizers (HAS) as one component of Recyclossorb 550, the influence of a benzotria-

zole UV absorber (Tinuvin 326) on the resulting performance was tested. For the repigmentation stage, two different pigments were used in form of masterbatch under the code names: Sicolen Blue pigment 22006 MB and Sicolen Red pigment 1115 MB. A double-arm kneading mixer from Werner Company, with sigma blades and mixing chamber of 1.50 L, was used for dry blending of the additives with the crate material (homogenization stage).

Remelting and MFR Retention

Reprocessing Procedure

The reprocessing procedure includes three different routes: (1) remelting of nonrestabilized material; (2) remelting of restabilized material using 0.2% w/w Recyclossorb 550; and (3) remelting of restabilized material using 0.4% w/w Recyclossorb 550.

For each of the aforementioned routes, five multiple extrusion cycles were performed with a Brabender Plasti-Corder PLE 330, single-screw laboratory extruder at NTUA. The screw length was 500 mm (L) and the diameter 20 mm (D), giving an effective length-to-diameter ratio of 25 (L/D). The extruder was heated at four zones at the cylinder and the die. Throughout all the multiple extrusion cycles, the screw rotation speed was kept at 50 rpm, yielding a throughput of around 0.8 kg/h.

To investigate the effect of the reprocessing temperature on melt flow rate (MFR) retention, the following five different remelting temperature ranges were applied: (1) max. 220°C (tempera-

Figure 7 HDPE crates, green material: effect of multiple extrusion on MFR at 250°C.

tures of the four zones: 190, 200, 210, 220°C); (2) max. 235°C (205, 215, 225, 235°C); (3) max. 250°C (220, 230, 240, 250°C); (4) max. 265°C (235, 245, 255, 265°C); and (5) max. 280°C (250, 260, 270, 280°C). For selected compositions, the influence of twin-screw extrusion (Werner & Pfleiderer ZSK 25, see below) was also checked.

Finally, as already mentioned, a repigmentation stage was applied to determine the effect of new pigments on the stability of repigmented crate material during reprocessing. For the purposes of this study, the reprocessing procedure was repeated while varying as above the nature of the restabilization added and the remelting temperature applied. Because the original crate ma-

terial was yellow, the blue pigment yielded green, and the red pigment produced orange.

MFR Measurements

Melt flow rate measurements were carried out for all grades prepared according to the procedure A of the ASTM D1238-73 or ISO 1133. The temperature was fixed at 190°C, and the weight of the ram (load) was equal to 2160 g. Samples weights varied from 3–3.5 g.

Mechanical Performance

Specimens Preparation

A Werner & Pfeiderer ZSK 25 twin-screw extruder and an Arburg 221-75-350 injection mold-

Figure 8 HDPE crates, orange material: effect of multiple extrusion on MFR at 250°C.

Table I   Twin-Screw Extrusion MFR (190°C/2.16 kg) According to ISO 1133

1	Temp. max. °C	Extrusion Cycles				
		2	3	4	5	
Nonrestabilized–nonrepigmented	250	1,49	—	—	—	—
0.4% Recyclossorb 550–nonrepigmented	250	3,66	—	—	—	—
0.4% Recyclossorb 550–nonrepigmented	265	3,57	1,66	1,56	1,31	1,38
Nonrestabilized–green repigmentation	250	2,26	—	—	—	—
0.4% Recyclossorb 550–green repigmentation	250	3,64	2,26	1,40	1,04	0,89
0.4% Recyclossorb 550–green repigmentation	265	1,86	1,17	0,93	0,93	0,98

ing machine were used for specimens preparation. Passing through the extruder ensures complete homogenization of the material. Specimens were prepared for both repigmented and non-repigmented material and in four different qualities: (1) nonrestabilized specimens; (2) restabilized with 0.2% w/w Recyclossorb 550; (3) restabilized with 0.4% Recyclossorb 550; and (4) restabilized with 0.2% Recyclossorb 550 and 0.1% Tinuvin 326.

The aforementioned machines are located in the Laboratories of Ciba Spezialitätenchemie Lampertheim GmbH at Lampertheim, Germany. They were employed to effect a faster production rate of all specimens needed. The working conditions of the twin-screw extruder was 100 rpm rotation speed and operation temperature at 250°C, and in the injection molding machine, temperature and pressure were kept at the levels of 245°C and 50 bar, respectively.

Tensile Impact Test

Tensile impact tests were carried out for all different grades according to the ISO 8256 or DIN 53 448 methods with an Zwick PSW 5101 tensile impact tester 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.

Tensile Test

Tensile tests were carried out using an Instron 4466 tensile machine according to D638-76 ASTM method in standard laboratory conditions, with a rate of extension equal to 50 mm/min.

RESULTS AND DISCUSSION

MFR Retention

Figures 1 to 3 illustrate the effect of the multiple extrusion cycles on MFR at three different re-

Figure 9   Tensile impact strength of recycled HDPE crates.

melting temperatures (220, 250, 280°C). In all cases, a reduction in MFR is observed after each successive extrusion, for both restabilized and nonrestabilized grades. This behavior could be possibly related to crosslinking phenomena occurring during reprocessing, indicating a Phillips-type HDPE crate material. It can also be seen that the nonrestabilized grade always presents the lower values. In other words, the addition of the restabilization system improves molecular weight retention; that is, processing stability, even after the last remelting cycle.

Figures 4 to 6 demonstrate the MFR differences between extrusion cycles, with remelting temperature increasing from 220 to 280°C. It becomes evident, that at the lower operation temperatures (220–235°C), the degradation of the crate material remains limited, especially for the restabilized grades. On the contrary, as the operation temperature further increases, polymer degradation is not negligible, but the restabilization level becomes a crucial parameter. Note that even at the higher reprocessing temperature of 280°C, the MFR difference between the first and the last extrusion cycle remains constant or nearly constant for the restabilized grades; whereas, in the nonrestabilized material, a considerable deviation is observed.

The effect of multiple extrusion on MFR for green and orange repigmentation are presented in Figures 7 and 8, respectively. Data at 250°C remelting temperature are presented. The data show that, even in this case, there is an MFR reduction after each extrusion cycle, caused by the crosslinking mechanism. It is a well-known fact that pigments are able to increase viscosity in the same way as fillers.[25] At equal parts by weight, the more finely dispersed pigments are generally more effective than fillers. However, because of the low concentration in which they are used, pigments have negligible influence on the melt viscosity of the polymeric material.[25] The latter seems to be the case for the aforementioned repigmentations. Within our experimental limits, the repigmented materials present a rheological behavior similar to the nonrepigmented material for both restabilized and nonrestabilized grades. It is important to mention that all data, at different remelting temperatures, also indicate the same trend.

Furthermore, the influence of the extrusion type (single screw, twin screw) must be discussed. As known, twin-screw extrusion is much more severe on polymer degradation than single screw.

Table II   Coefficient of Variation Values for the Tensile Impact Test

Restabilization–Repigmentation	Coefficient of Variation
Nonrestabilized–nonrepigmented	2,11
0,2% Rec. 550–nonrepigmented	0,59
0,4% Rec. 550–nonrepigmented	1,23
0,2% Rec. 550 + Tin. 326–nonrepigmented	1,49
Nonrestabilized–green	1,47
0,2% Rec. 550–green	1,53
0,4% Rec. 550–green	1,41
0,2% Rec. 550 + Tin. 326–green	0,95
Nonrestabilized–orange	1,92
0,2% Rec. 550–orange	0,72
0,4% Rec. 550–orange	0,63
0,2% Rec. 550 + Tin. 326–orange	0,74

This fact is confirmed by the data in Table I in comparison to data from Figures 1 to 3. It follows, again, that restabilization is essential for maintaining the properties.

Mechanical Performance

Figure 9 demonstrates the tensile impact strength of restabilized and nonrestabilized grades for all three repigmentations. There is a slight indication that the tensile impact strength decreases, while increasing the stabilization level. Coefficient of variation values presented in Table II, seem to confirm the trend observed. This phenomenon could be possibly attributed to crosslinking. Increased crosslinking yields harder and stiffer material.[26] Because crosslinking is more severe in the nonrestabilized material, it becomes evident that this material presents the most compact structure, resulting in some improvement of the tensile impact strength performance.

The aforementioned hypothesis, based on tensile impact strength data, can also explain the trend of the tensile strength presented in Figure 10. In all cases, for both repigmented and nonrepigmented material, the data suggest, that there is, again, a slight improvement in the tensile strength of the nonrestabilized grades. This

Figure 10 Tensile strength of recycled HDPE crates.

could also be correlated with the stiffer structure of this material.

The elongation at break for all the recycled qualities is shown in Figure 11. In all cases, a significant increase of the elongation at break is observed for the restabilized grades. This can be explained by the well-known fact that elongation at break decreases with crosslinking. In other words, branching of the nonrestabilized material, leading to limitation in the free volume between the polymer chains and to an embrittlement increase, could be possibly the reason for poor extensibility. However, after the addition of the restabilization system no significant crosslinking occurs, allowing the polymer chains to extend much more freely in a tensile mode experiment.

Turning now to the repigmentation aspects, the addition of the new pigments results in a remarkable improvement in the elongation of the original material. It can be assumed that this addition affects the morphology of the material; that is, the amount of crystallinity, the size, and the distribution of the spherulites, or that a plasticization effect is faced, improving extensibility. Figure 12 presents the modulus of elasticity for each of the aforementioned grades. In this case, no significant and systematic changes are noticed.

Figure 11 Elongation at break of recycled HDPE crates.

Figure 12 Modulus of elasticity of recycled HDPE crates.

CONCLUSIONS

The remelting–restabilization technique is applied for recycling of postused, yellow-pigmented, HDPE bottle crates. During the reprocessing procedure, the crate material suffers from degradation, caused by well-known crosslinking and branching phenomena along the polymer structure. However, the addition of the restabilization system significantly improves processing stability during repeated remelting cycles. Moreover, as the reprocessing temperature varies, the restabilized grades exhibit a remarkable stability against degradation, but at the higher temperatures, the restabilization level becomes crucial.

The mechanical tests show that the addition of the restabilization system is mandatory for elongation improvement. Furthermore, the addition of the pigments tested in the original material (repigmentation stage) seems to have a negligible effect on the melt viscosity and on the mechanical properties tested, with the exception of the tensile elongation, where, again, a significant improvement is observed. The results on processing of bottle crate recyclate will be completed through heat aging and artificial weathering experiments.

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