

# Effect of Hydroperoxide Decomposer and Slipping Agent on Recycling of Polypropylene

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Received 20 June 2003; accepted 19 December 2003

**ABSTRACT:** Polypropylene (PP) recycling has always been challenging because the polymer is highly susceptible to thermooxidative degradation during extrusion. Recycled (degraded) PP is normally blended with virgin PP to achieve reasonable mechanical properties after reprocessing operations. However, impurities present in recycled PP tend to degrade even the virgin PP in this process. In this study, standard recycled PP was produced in a laboratory by repeated extrusion and pelletization operations of virgin PP. This material was blended with virgin PP in a ratio from 3 : 7 to 7 : 3. An attempt was made to stabilize the recycled blend by adding a peroxide decomposer (triphenylphosphite, TPP) and a slipping agent (zinc stearate) in contrast to radical scavengers normally used in reprocessing. It was

found that by using 0.3–0.5 wt % of TPP and 2 wt % of zinc stearate, this degradation could be effectively attested. Compared to the tensile strength retention of 68% (based on strength of pure virgin PP) of a 60 : 40 (recycled : virgin) PP blend without any stabilizer, a value of 77% was obtained for the same blend with the above-mentioned stabilizers. This stabilization effect was attributed to decomposition of unstable hydroperoxides to stable compounds in the recycled materials by TPP, and lower generation of new radicals in the presence of zinc stearate. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3247–3251, 2004

**Key words:** poly(propylene); recycling; stabilization; degradation; triphenylphosphite

## INTRODUCTION

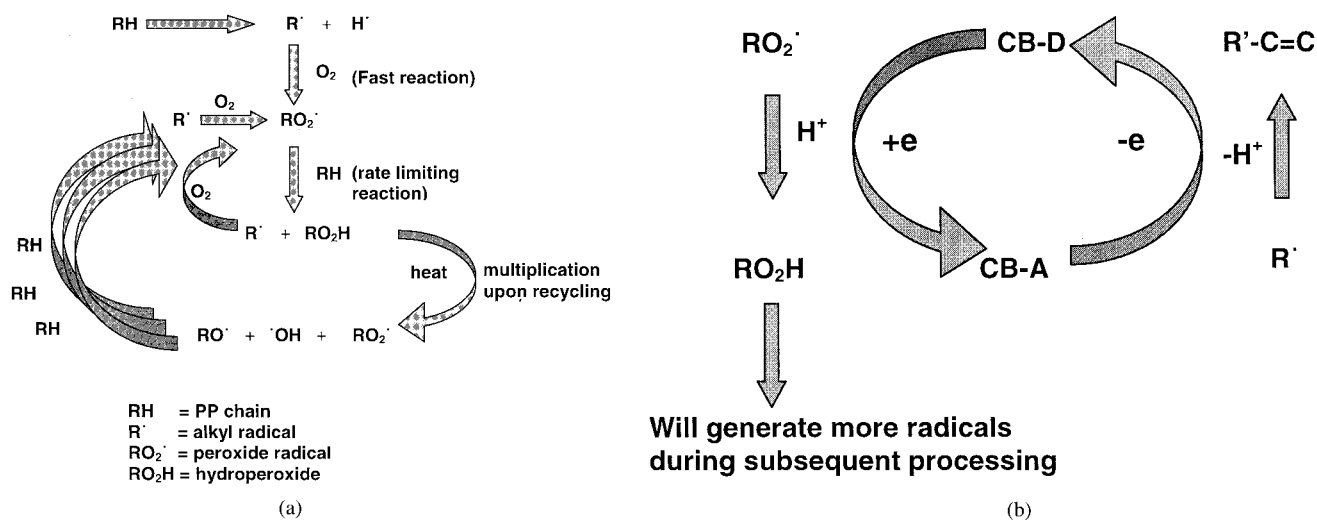
Disposal of polypropylene (PP) is becoming increasingly difficult for the plastic industry. Although its disposal is inevitable at the end, it is highly desirable that its useful life is extended by recycling the polymer several times. This is a challenge because PP is highly sensitive to thermooxidative degradation during processing and to photooxidative degradation during use. Virgin PP is reasonably stable because of nonavailability of radicals or ketone groups in the fresh material. However, on every recycling, the amount of radicals and reactive carbonyl sites increases dramatically. This poses a formidable task in stabilizing the PP during reprocessing and finally in use. Many commercial stabilizers are available to capture radicals present in the polymer. Some of the examples<sup>1–4</sup> are Irganox 565 and 1010, Tinuvin 622, 770 DFD, and Chimassorb 944, which belong to the class of stearically hindered phenols and aromatic amines. Triazines<sup>3,5,6</sup> were also shown to stabilize PP. However, these stabilizers are expensive and increase the cost of PP reprocessing by a significant value. It is highly desirable that the effect of readily available low-cost compounds may be eval-

uated to determine the effectiveness of such compounds on stabilization of recycled PP.

The first stage of degradation occurs during the first processing of PP inside an extruder when the polymer is subjected to high-shear stresses at high temperature. Radicals are generated because of the scission of polymer chains.<sup>7,8</sup> These alkyl radicals react readily with oxygen to form alkyl peroxide radicals.<sup>9</sup> Because of the easy availability of trapped or dissolved oxygen in recycled PP, this transformation is predominant. This results in a much higher concentration of alkyl peroxide radical than alkyl radical. Alkyl peroxide radical is therefore the main species used to propagate chain scission in the rest of the polymer. The radical transfers from one chain to another by abstraction of hydrogen and results in hydroperoxide formation. Hydroperoxide being unstable under heat or light (i.e., reextrusion conditions and use) leads to the formation of more radicals, and the number of radical species multiplies.<sup>10,11</sup> This cycle, as depicted in Figure 1(a), repeats over and over again during melt processing, resulting in polymer chain degradation.<sup>12</sup>

The stabilization of alkyl peroxide radicals in PP requires the addition of chain breaking donors/acceptors such as stearically hindered phenols and aromatic amines.<sup>13,14</sup> These compounds capture the radical from alkyl peroxide and convert it into hydroperoxide compounds [Fig. 1(b)]. These stabilizers were shown to be effective in reducing the rate of aging at the used temperatures. However, the products of the above

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**Figure 1** The schematic diagram of the (a) mechanism of degradation of PP (b) stabilization by chain breaking acceptor and donor agents.

reactions, hydroperoxides, remain in the processed polymer and undergo scission during reprocessing/heating (recycling) to generate twice the amount of radicals. In this way, the actual cycle is not broken and the degradation may continue in subsequent processing steps. Therefore, it may be concluded that to get effective stabilization during recycling, hydroperoxide compounds must be decomposed.

Phosphorous compounds such as aryl phosphite function as hydroperoxide decomposer and are conventionally recommended as costabilizers during first processing of the virgin (fresh) PP. However, not much attention has been conferred on the role of hydroperoxide decomposers in recycling of the PP. This study was carried out to evaluate the use of hydroperoxide decomposers as low-cost primary stabilizers in recycled PP. Further, the effect of chain slipping agents such as zinc stearate during recycling had been evaluated without and in combination with peroxide decomposers.

## EXPERIMENTAL

### Materials

Virgin PP grade H020SG was purchased from Reliance Industries Ltd. (Mumbai, India). Standard degraded PP samples were prepared by extruding and palletizing the above material up to four times by using a Klockner Windsor extruder fitted with a strand die. Water was used as the quenching medium. After palletizing, the chips were dried in a vacuum oven at 100°C for 24 h.

### Melt flow index

The palletized and dried sample chips were analyzed for MFI by using a MFI tester (International Equip-

ments, Bombay, India) under standard conditions of 230°C and a load of 2.16 kg.

### Blend preparation

Five blends of virgin PP with degraded PP were made as described in Table I. The chips were mixed physically by using a tumbler mixer and then extruded by using a single-screw Klockner Windsor extrusion line at the same conditions as mentioned above. After quenching, the extruded strand was palletized and dried as described before. The additives such as triphenylphosphite (TPP) and zinc stearate were physically blended before extrusion at predetermined concentrations, as indicated in Table I.

### Spinning of PP filaments

The sample chips were melt-spun on Klockner Windsor extrusion line at 230°C and quenched in water bath

**TABLE I**  
Details of Samples Prepared

Sample no.	4× Recycled PP	Virgin PP	TPP	Zn St.
Blending and extrusion of PP without stabilizers				
1	100	0		
2	70	30		
3	60	40		
4	50	50		
5	30	70		
6	0	100		
Blending and extrusion of PP with stabilizers				
7	60	40	0.1	
8	60	40	0.3	
9	60	40	0.5	
10	60	40	0.5	2.0
11	60	40		2.0

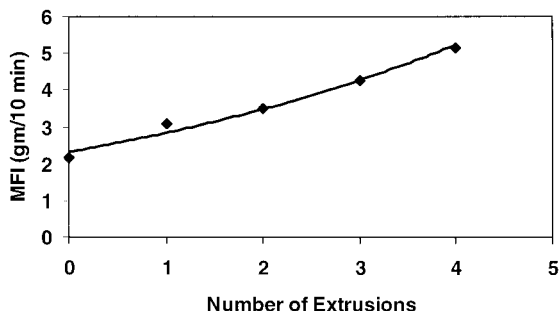


Figure 2 Effect of number of recycling extrusions on melt flow index (MFI) of PP.

maintained at 15°C. The extruded filaments were drawn on a two-stage drawing machine with a heater plate temperature at 70°C and heated center godet at 60°C. The draw ratio used was 5.0 (=4.0 × 1.25) for all samples. The filaments obtained were tested for mechanical properties.

**Tensile properties**

The spun and drawn filaments were tested on an Instron 4202 tensile tester. The gauge length was 10 cm and crosshead speed was 250 mm/min.

**RESULTS AND DISCUSSION**

**Preparation of standard recycled PP**

The standard recycled material was prepared by carefully reprocessing the virgin material up to four times in a standard laboratory extrusion line. The melt flow index (MFI) of the virgin and reprocessed samples are plotted in Figure 2. The virgin sample was found to have an MFI of 2.17 g/10 min, which increased to 5.13 after four recycling extrusions. The MFI increased nearly linearly with the number of extrusions. The increase in MFI is a direct indication of reduction in molecular weight due to chain scission, as explain earlier in Figure 1. Figure 3 represents the change in

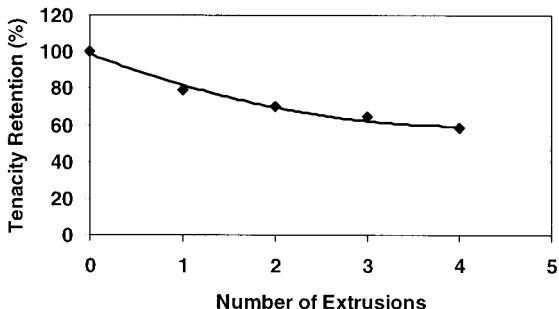


Figure 3 Effect of number of recycling extrusions on tensile properties of PP.

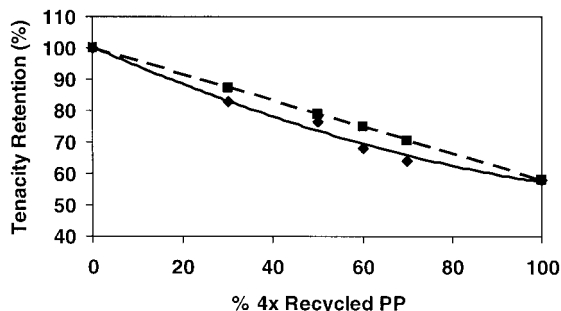


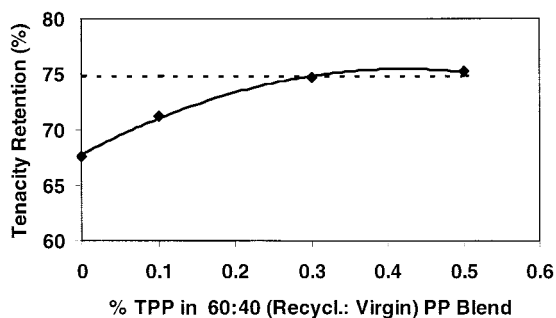
Figure 4 Effect of blending of virgin PP with four-times recycled PP on mechanical properties of the blend. (◆) Experimental values; (- - ■ - -) theoretical values obtained using additive model.

tensile strength of the PP filament yarn prepared from virgin and recycled materials. As was expected, the tensile strength of the filaments from recycled materials with four extrusions drops to 58% of the virgin value. It is interesting to note that the drop in tenacity is steepest for the first extrusion. Tenacity dropped by about 20% after the first recycling. Thereafter, the drop was comparatively smaller with every subsequent extrusion.

**Effect of virgin PP on blends**

The normal practice of utilizing recycled polymer is to blend it with virgin material. This ensures availability of higher molecular weight polymer chains to compensate for the strength loss in recycled material. However, in the case of PP, this may lead to the degradation of the virgin material itself because of the copresence of the recycled material, which has a high concentration of radicals and hydroperoxide groups. Figure 4 depicts the effect of the addition of recycled PP in virgin PP on tensile strength retention of the blend. The recycled PP used was the one processed four times. The tensile retention is calculated on the basis of control sample produced from virgin PP. The presence of virgin PP improved the mechanical properties of the blend. The amount of improvement was found to be dependent upon the weight percent of virgin PP.

The best expected scenario in a physical blend is an additive contribution of the properties. If the tensile properties are modeled on the basis of the additive rule, a straight line joining the pure virgin and pure recycled PP can be created. As can be seen from the figure, the experimental values of strength retention are lower by 5–10% from the modeled values. This indicated that the contribution from the virgin polymer is affected because of a degenerative effect of the radicals and hydroperoxides present in the blend.



**Figure 5** Effect of triphenylphosphite on tenacity retention values of the 60:40 (recycled:virgin) PP blend. (◆) Experimental values; (- - -) target theoretical value obtained using additive rule for the blend.

### Effect of stabilizers on recycled virgin blend

To counter the degradative effect, chain breaking donor or acceptor or redox stabilizers are normally recommended. These compounds are expected to capture the alkyl radicals or alkyl peroxide radical and arrest the effect. However, the hydroperoxide compounds that are formed because of this action remain and being unstable create a greater number of radicals during subsequent processing. Therefore, an alternative approach was formulated where instead of the above compounds, TPP was added in the blend during processing. This compound was expected to stabilize the blend by decomposing the hydroperoxide compounds into stable species that do not undergo radical generation. In this way, the radical multiplication (branching) cycle was expected to be broken. Figure 5 is a plot between the tensile strength retention of the 60 : 40 (recycled : virgin) PP blend with percentage addition of TPP. As may be noted from the figure, significant stabilization, indicated by an increase in strength retention from 68 to 75%, was achieved with a small addition of TPP. A maximum value of 75% was achieved with 0.3–0.5 wt % of TPP. When compared to the additive contribution modeled value from Figure 4 (shown as dashed straight line in Fig. 5), this value was found to match the ideal value. This indicated that the addition of a peroxide decomposer could effectively arrest the cyclic degradation mechanism and degenerative contribution of recycled material on virgin PP.

In any processing, new alkyl radicals are generated because of thermomechanical shear among the polymer chains and with the mechanical component. This generation of new radicals may be reduced by use of a slipping agent such as zinc stearate, which does not allow the critical stresses to build up. This effect is well documented in the literature.<sup>15,16</sup> However, their usefulness in recycling operations is not known. Table II depicts the value of tensile strength retention of the 60 : 40 (recycled : virgin) PP blend when zinc stearate was

added at 2 wt %. The strength retention increased nominally from 68 to 71%. This result showed that even at a very high concentration of 2 wt %, although stearate was able to improve the strength retention by reducing new radical generation, it was not able to counter the degradative effect of hydroperoxide compounds. However, interestingly, in presence of 0.5 wt % TPP, the addition of zinc stearate (2 wt %) in the blend could further improve the strength retention values to 77% (Table II). This is about a 9% increase over the values for nonstabilized blend.

This improvement has significant commercial implication on blended PP processing. The use of simple compounds such as TPP and zinc stearate may favorably lower the use of virgin PP in recycled virgin blends while obtaining mechanical properties shown by virgin-enriched blends. In this study, 60 : 40 (recycled : virgin) blend with TPP and ZnSt has shown tensile strength values comparable to a nonstabilized blend of 44 : 56 (recycled : virgin) blend. This amounts to a reduction of 16% by weight of virgin PP in the above case.

The above increase in tensile strength retention values may be compared with those given in the literature<sup>17,18</sup> for recycled blends by using commercially available stabilizers such as Irganox 1010, Irgafos 168, and Tinuvin 770 DFD. The hydroperoxide decomposer TPP and chain slipping agent combination was found to be either the same or a little better. In relation to the cost, the compounds used in this study are significantly cheaper than the commercial stabilizers mentioned above.

### CONCLUSION

In this study, recycling of PP was studied in the presence of peroxide decomposers and slipping agents. Toward this end, standard recycled PP samples were created in the laboratory to simulate recycling of PP. The recycled PP chips were blended with virgin PP to establish the effect of unstable reactive species inside the recycled PP on the virgin PP in the blend. It was observed that when no stabilizers are used, the recycled PP has a degenerative effect on the virgin PP and the mechanical properties of the blend are found to be

**TABLE II**  
Effect of Zinc Stearate on the Mechanical Properties of 60 : 40 (recycled : virgin) PP Blend

Sample No.	TPP	Zn St.	Tensile Strength Retention (%)
3	0.0	0.0	68
11	0.0	2.0	71
9	0.5	0.0	75
10	0.5	2.0	77

lower than those expected from an additive blend model. However, the use of peroxide decomposer TPP was found to reduce this effect significantly and arrest most of the degeneration with 0.3–0.5 wt % of TPP in the blend. Use of zinc stearate, a slipping agent, was found to provide additional protection by reducing the generation of new radicals during reprocessing.

From this investigation, it may be concluded that the presence of hydroperoxide compounds has a degenerative influence on recycling of PP, and therefore, decomposition of these compounds may be most important to get adequate stabilization. The use of TPP and zinc stearate was found to result in saving of the virgin PP required to attain a predetermined mechanical performance from the recycled virgin blend. The effect of these compounds was found to be comparable or even better than the commercially recommended mix of expensive stabilizers. The low cost and excellent effectiveness of these compounds hold great promise for their use in PP recycling.

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