Stabilization of Thermoplastic Resins by Using Sumilizer®GP

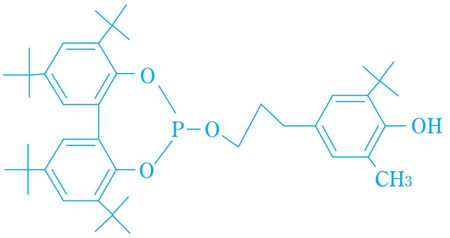
Sumitomo Chemical Co., Ltd.
Fine Chemicals Research Laboratory
Kenji KIMURA
Hideaki AWA
Naoki INUI

Sumilizer®GP, which has a unique structure with both a phenolic antioxidant moiety and a phosphonic antioxidant moiety in a single molecule, can efficiently prevent degradation of thermoplastic resins during processing. In this review, the possibility of new applications for thermoplastic resins is introduced, as well as stabilization of thermoplastic resins, such as polyolefin resins, polystyrene resins and so on, is introduced during processing.

This paper is translated from R&D Report, “SUMITOMO KAGAKU”, vol. 2006-I.

Introduction

Sumilizer®GP (abbreviated as GP hereafter) is a high performance hybrid process stabilizer that Sumitomo Chemical developed and launched in 2000 as an inhibitor against fish eye gel, which occasionally occurs when processing linear low density polyethylene. As **Fig. 1** shows, the hybrid process stabilizer introduced in this paper is the world's first stabilizer in which a phenolic antioxidant structure and a phosphonic antioxidant structure have both been introduced into a single molecule. It means that this is a high performance process stabilizer that demonstrates an intramolecular synergistic effect. In a conventional antioxidant (process stabilizer), several antioxidants (process stabilizers) were combined and added to resins. However, GP can be utilized as it is, without any other antioxidants. Moreover, GP can demonstrate higher process stabilization performance than that of conventional antioxidants (process stabilizers) when comparing the same quantities. Thus, if similar stabilization performance is satisfactory, the quantity of GP required can be smaller than that of a conventional antioxidant required, resulting in better cost efficiency.[1), 2)] Furthermore, with respect to the unfavorable effects derived from adding an antioxidant (process stabilizer) (for example, NOx discoloration, blooming, hydrolysis due to long-term storage), GP has excellent resistance to NOx discoloration and outstanding compatibility with polyolefins. It is also highly resistant to hydrolysis.[1), 2)] **Fig. 2** shows these special features of GP. Having these advantages, GP has started to account for a large share of the domestic market for linear low density polyethylene stabilizers within only 5 years of its market launch.



$C_{42}H_{61}O_4P$
Exact Mass : 660.43
Mol. Wt. : 660.91
C, 76.33 ; H, 9.30 ; O, 9.68 ; P, 4.69

Fig. 1 Structure of Sumilizer®GP

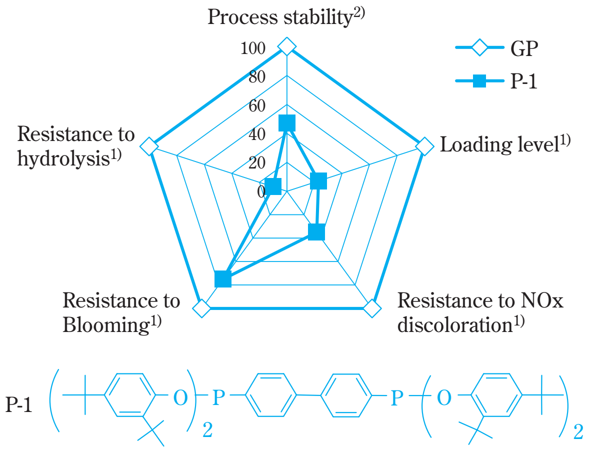
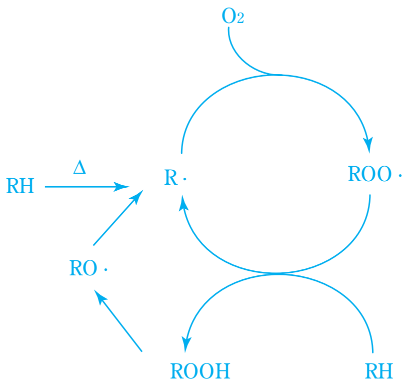


Fig. 2 Typical Performance of GP for LLDPE

In this paper, the degradation and stabilization mechanisms of thermoplastic resins (polyolefins) will be explained. Then more specific examination cases of the following factors will be introduced: improvement in physical properties of thermoplastic resins other than polyethylene when GP is utilized; and potential GP applications. Lastly, precautions to be taken for GP usage will be explained.

Degradation Mechanisms of Thermoplastic Resins (Polyolefins)

Polyolefins are often utilized as study subjects when conducting research on degradation mechanisms of thermoplastic resins. **Scheme 1** shows general degradation mechanisms of polyolefins.[3)]

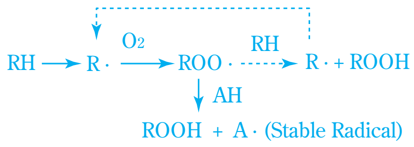


Scheme 1 Autoxidation Mechanism

Polyolefins (RH) produce active alkyl radicals (R·) due to the action of light and heat. When dissolved oxygen (O_2) is present in polyolefins and its concentration is sufficient, alkyl radicals react with oxygen and produce peroxy radicals (ROO·). These peroxy radicals then extract hydrogen (H) from other polyolefin molecules and reproduce alkyl radicals while at the same time producing hydroperoxides (ROOH). Thus, once active alkyl radicals have been produced within a polyolefin, degradation of the polyolefin automatically progresses in a chain reaction. For this reason, the mechanism is referred to as the "autoxidation mechanism" of polyolefins.

Stabilization Mechanisms of Thermoplastic Resins (Polyolefins)

In order to prevent degradation of polyolefins, it is important to break the above-mentioned chain cycle. With this in mind, a phenolic antioxidant is added to the resin (**Scheme 2**).



Scheme 2 Stabilization Mechanism of Hindered Phenolic Antioxidant (AH)

Hydrogen (H) is supplied by the phenolic antioxidant (AH) to a peroxy radical produced from the polyolefin. The peroxy radical then forms a metastable hydroperoxide, thus allowing the phenolic antioxidant to become a stable phenoxy radical, resulting in process stabilization.[4)]

Since the metastable hydroperoxide that has been produced during the above process reproduces active hydroxy and alkoxy radicals due to heat, the hydroperoxide can be further stabilized by reducing it to a stable alcohol. Based on this concept, phosphonic process stabilizers and thio-propionic antioxidants are used in thermoplastic resins such as polyolefins, as well as phenolic antioxidants (**Scheme 3**).[4)]

Scheme 3 Stabilization Mechanism of Secondary Antioxidant (B)

Both phosphonic process stabilizers and thio-propionic antioxidants are secondary antioxiants, and both antioxdants have the function of reducing hydroperoxides to alcohols. Since phosphonic process stabilizers demonstrate stoichiometric hydroperoxide reduction at high temperatures, they are often utilized as process stabilizers for thermoplastic resins. On the other hand, it is known that thio-propionic antioxidants have the function of decomposing acid catalyst hydroperoxides and that they are highly effective in reducing degradation of thermoplastic resins. Therefore, they are often used as antioxidants for thermoplastic resins.[4)]

GP introduced in this paper is a high performance process stabilizer possessing a unique structure in which both a phenolic antioxidant moiety and a phosphonic process stabilizer moiety are present in a single molecule. Their molecular design is based on the aforementioned stabilization mechanism. In other words, when using both phenolic antioxidants and phosphonic process stabilizers, hydrogen is supplied from the phenolic antioxidant, thus producing a metastable hydroperoxide. This hydroperoxide is then reduced to an alcohol by the phosphonic process stabilizer. However, there is a degree of probability that the hydroperoxide will be decomposed to active species such as hydroxy or alkoxy radicals due to heat. However, as GP has both phenolic and phosphonic moieties in a single molecule, it can be assumed that the hydroperoxide produced from the peroxy radical is immediately reduced to an alcohol due to the presence of the phosphonic moiety. Thus, it can be concluded that GP's process stabilization effect becomes synergistically higher than containing both a phenolic antioxidant and a phosphonic process stabilizer.[1)]

Stabilization of Polypropylene (PP)

1. Polypropylene (PP) Targets

One of the primary applications of polypropylene (PP) is use in packaging materials (films). For this PP application, high melt tension is required for stability during the film formation process, as well as a high MFR to achieve workability. Therefore, PP is often utilized for packaging films, as it has a wide range of molecular weight distribution, from ultrahigh molecular weights to relatively low molecular weights, depending upon the physical properties required. However, when producing film from PP with ultrahigh molecular weights, it can be observed that molecular breakage tends to occur, resulting in a significant reduction of its melt tension.

2. Improving the Balance Between MFR and Melt Tension of Polypropylene (PP) Using GP

Fig. 3 shows the results of tests examining the balance between MFR and high melt tension.[5)] Before conducting the test, molecular breakage of PP with ultrahigh molecular weight was effectively reduced during the film processing.

While GP is added to PP and the PP demonstrates high melt tension (around 3g) after the melt extrusion process, both phenolic antioxidant (AO-2) and phosphonic process stabilizer (P-2) are added to PP and the PP demonstrates decrease melt tension (to 1g) after the melt extrusion process.

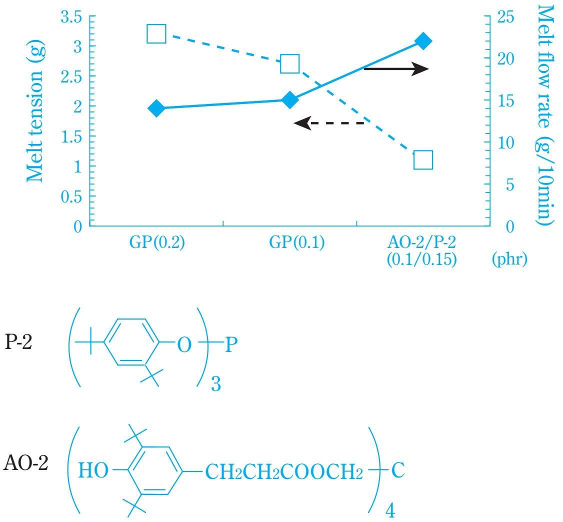


Fig. 3 Balance of Melt flow rate and Melt tension of PP

With respect to MFR, it still remains around 14 – 15g/10min for the GP-added PP even after melt extrusion has been performed. The result suggests that the MFRs of both PP that contains a phenolic antioxidant (AO-2) and PP that contains a phosphonic process stabilizer (P-2) increase to around 22g/10min. It can be assumed that this is because GP can effectively control molecular breakage when processing PP with ultrahigh molecular weight.

Therefore, the result indicates that GP-added PP with a wide range of molecular weight distribution (from ultrahigh molecular weight to a relatively low molecular weight) has outstanding film production stability.

Stabilization of Polystyrene (PS)

1. Polystyrene (PS) Targets

Resin pellets can be obtained from polystyrene (PS) through degassing and extrusion processes after polymerization has been performed. These pellets contain small amounts of dimers and trimers of styrene monomer. These dimers and trimers can cause discoloration and can decrease resistance to heat of styrene-based resins. Therefore, it is necessary to minimize dimer and trimer residues.

2. Reducing Dimers and Trimers in Polystyrene (PS) Using GP

After polymerization of styrene monomers using a polymerization initiator, PS pellets can be obtained via a degassing process. **Fig. 4** depicts the result of total concentration of dimers and trimers contained within PS pellets, measured using gas chromatography.[6)]

Total content of dimers and trimers within PS pellets obtained through the following procedures ranges

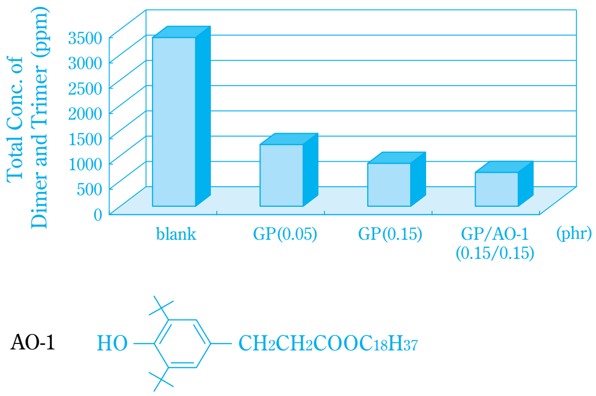


Fig. 4 Total concentration of Dimer and Trimer after PS production

from 700 to 1200 ppm: At first, GP is added to the PS after polymerizing styrene monomers using a polymerization initiator. Then degassing and extrusion processing are performed. Conversely, when GP is not added to the PS, total content of dimers and trimers within the PS pellets exceeds 3,000 ppm. Thus, it is obvious that adding GP reduces the content of dimers and trimers.

3. Improving Polystyrene (PS) by Reducing Dimers and Trimers

We conducted the following measurement test for MFR and yellowness index (ΔYI) of PS pellets obtained from the procedures described in the section above: the PS pellets were extruded 5 times at 220°C. Next, the MFR and yellowness index of the pellets before and after these extrusions were measured. **Fig. 5** shows the test results.$^{6)}$

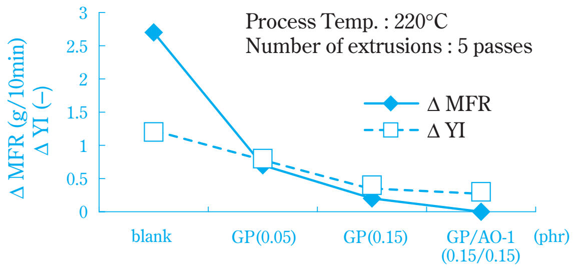


Fig. 5 Stabilization of PS during processing

From the results, it is obvious that heat stability was improved (ΔMFR is small) for the PS pellets in which dimer and trimer residues have been reduced using GP. Resistance to discoloration (ΔYI is small) of these PS pellets was also improved. Thus, the results suggest that adding GP to PS can improve resistance to heat and resistance to discoloration of the PS.

Stabilization of MS Resins (MS)

1. MS Resins (MS) Targets

MS resins have high transparency. Due to this characteristic, these resins have been utilized in the field of optics, such as diffusion plates. However, compared to other optical resins such as PMMA, the degree of yellowing that occurs during the processing is slightly larger in MS resins. Therefore, if this disadvantage is improved, areas of MS resin application should expand further.

2. Improving Resistance to Thermal Discoloration of MS Resins Using GP

We conducted a kneading test on a MS resin using a Brabender Plastgraph as an experimental model for discoloration during the processing. The yellowness index (ΔYI) was measured at 230°C before and after the kneading operation (kneaded for 30 minutes) and the thermal discoloration was evaluated. **Fig. 6** shows the test results.

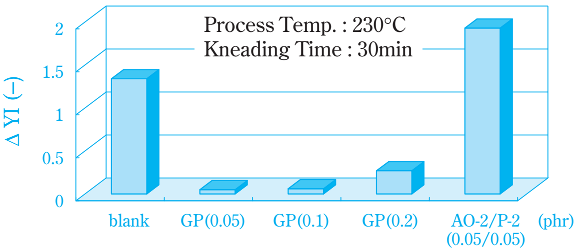


Fig. 6 Color stability of MS resin during processing

In the resin containing both a phenolic antioxidant (AO-2) and a phosphonic process stabilizer (P-2), the yellowness index (ΔYI) before and after the kneading operation (kneaded for 30 minutes) was larger than the resin with no additives, which means that the change in yellowing in the resin with no additives was large. Conversely, the resin containing GP showed almost no change in yellowing before and after the kneading operation (kneaded for 30 minutes).

3. Improving Resistance to Thermal Oxidation of MS Resins Using GP

Furthermore, resistance to thermal oxidation is also required in MS resins, as well as resistance to thermal discoloration. This is because MS resins come into contact with air at high temperatures during the extrusion process of large resin sheets. Therefore, the time required for oxidation (time to oxidation) was estimated using DSC and the resistance to thermal oxidation of the MS resin was then evaluated. The longer the "time to oxidation" is, the greater is the resistance to thermal oxidation. **Fig. 7** shows the test results.

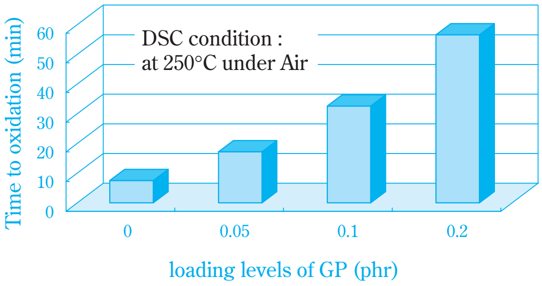


Fig. 7 Resistance to oxidation of MS resin

The time required for oxidation becomes longer in proportion to the amount of GP in the resin, indicating that the resistance to thermal oxidation of the resin increases in proportion to the amount of GP added to the resin.

4. Effect of GP on Resistance to Light of MS Resins

Since MS resins are used in the field of optics, it is necessary to verify the effect of GP on resistance to light of the resins, particularly resistance to light discoloration. **Fig. 8** shows the results of a resistance to discoloration test exposing the resin to light in XeWOM.

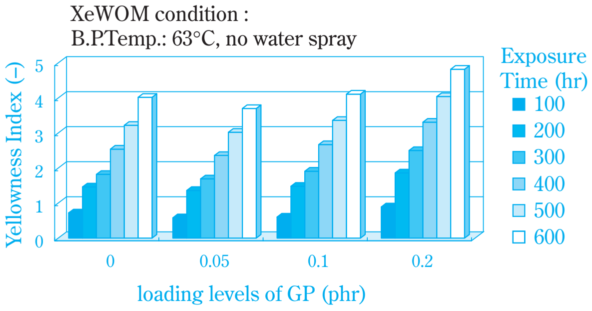


Fig. 8 Resistance to light discoloration of MS resin

Although it can be observed that there is a tendency for the resistance to discoloration to slightly decrease as the amount of GP increases, if the amount is under 1,000 ppm, there is almost no effect.

Thus, the results suggest that adding GP to MS resins may expand areas of application in the field of optics, particularly in areas where it was previously difficult to apply due to thermal discoloration.

Precautions to be Taken When Using GP

As described in the sections above, GP is a high performance process stabilizer with wide ranging potential. However, as its research progresses, we have discovered the characteristics introduced below. Because of these characteristics, precautions must be taken when using GP.

1. When Using Anti-blocking Agents with high solid acid strength with GP

Although GP has the characteristic that is not susceptible to hydrolysis under neutral conditions, it is more susceptible to hydrolysis under acidic conditions, in the same way as other phosphonic antioxidants (for example, P-2). **Fig. 9** shows the results of tests to observe the stability of GP kneaded into polyethylene containing a variety of anti-blocking agents (ABA).[7)]

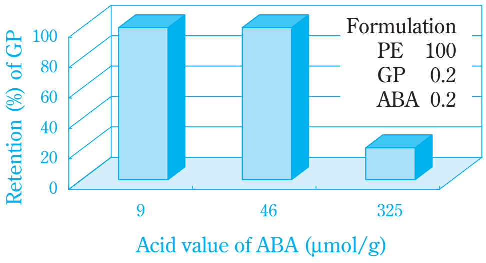


Fig. 9 Resistance to hydrolysis of GP under presence of anti-blocking agent during holding at 50°C in 80% R.H. for 7 days

When using an anti-blocking agent with high solid acid strength, hydrolysis of the GP progresses in the polyethylene. Thus, it is necessary to carefully select an ABA for GP, as with other phosphonic antioxidants.

Also, we have examined a method to improve resistance to hydrolysis for GP when an ABA that has high solid acid strength must be utilized. Assuming that this hydrolysis is caused by acid, we have examined the possibility of improving resistance to hydrolysis for GP when a neutralizer is being used as well. **Fig. 10** depicts the results of tests examining the possibility of improving resistance to hydrolysis for GP in the presence of a neutralizer.

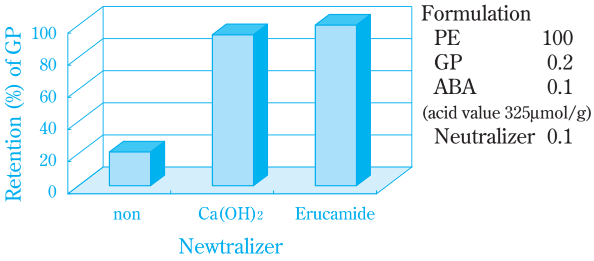


Fig. 10 Resistance to hydrolysis of GP under presence of anti-blocking agent and neutralizer during holding at 50°C in 80% R.H. for 7 days

As shown in Fig. 10, adding a neutralizer improves the resistance to hydrolysis for GP.

2. Thermoplastic Resins Containing High Concentrations of GP (Master Batch of GP)

Fig. 11 shows the results of a study on the relationship between concentration and resistance to hydrolysis for GP contained in polyethylene.

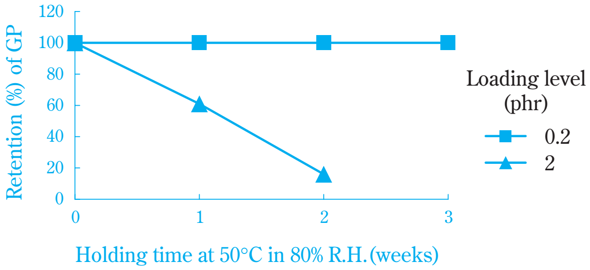


Fig. 11 Resistance to hydrolysis of GP in PE

As shown in Fig. 11, as the concentration of GP becomes higher, the resistance to hydrolysis for GP in polyethylene significantly decreases. We have assumed that this is because when hydrolysis occurs in GP, it produces phosphoric acid, thus increasing the acidic components within the resin, resulting in acceleration of the hydrolysis. In other words, while the amount of phosphoric acid derived from hydrolysis is small when the GP concentration is low, when the GP concentration is high, the amount of phosphoric acid derived from hydrolysis is large, thus accelerating the hydrolysis.

As with ABA, adding a neutralizer may improve the resistance to hydrolysis for GP. **Fig. 12** depicts the test results for improving resistance to hydrolysis.

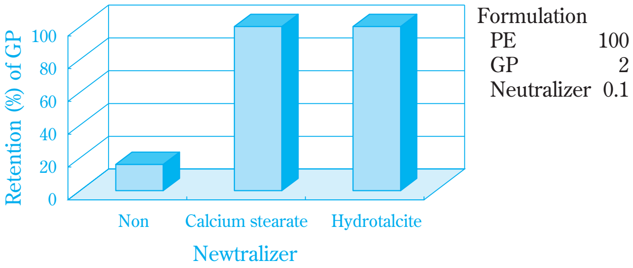


Fig. 12 Resistance to hydrolysis of GP under presence of neutralizer during holding at 50°C in 80% R.H. for 14 days

As expected, the test results indicate that adding a neutralizer improves the resistance to hydrolysis, even though the GP concentration is high in the resin.

Conclusion

When GP was first developed, it was used only as a stabilizer for linear low density polyethylene. However, as research advances, we see the possibility of expansion in its areas of application. We shall continue to strive to expand areas of application of GP with wide-ranging potential for thermoplastic resin materials through our further in depth research.

References

1) Fumitoshi Kojima, Kanako Fukuda, Kunihito Miyake, SUMITOMO KAGAKU, **2002-Ⅱ**, 42 (2002).
2) Fumitoshi Kojima, SUMITOMO KAGAKU, **2004-Ⅰ**, 24 (2004).
3) J. Pospisil and P. P. Klemchuk, “Oxidation Inhibition in Organic Materials Vol.1”, CRC Press Inc., (1990), p.1.
4) J. Pospisil, “Oxidation Inhibition in Organic Materials Vol.1”, CRC Press Inc., (1990), p.33.
5) Sumitomo Chemical Co., Ltd., JP 2003-73507 (2003).
6) Sumitomo Chemical Co., Ltd., JP 2002-179726 (2002).
7) Sumitomo Chemical Co., Ltd., JP 2005-272827 (2005).

PROFILE

Kenji *Kimura*

Sumitomo Chemical Co., Ltd.
Fine Chemicals Research Laboratory
Senior Research Associate

Naoki *Inui*

Sumitomo Chemical Co., Ltd.
Fine Chemicals Research Laboratory
Group Manager
Senior Research Associate

Hideaki *Awa*

Sumitomo Chemical Co., Ltd.
Fine Chemicals Research Laboratory
Researcher