Evaluation of an Aromatic Amine Antioxidant in Glass-filled Poly(propylene)

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Abstract

Glass-mat reinforced thermoplastic (GMT) composites have increasingly begun to replace traditional sheet molding compounds in automotive applications, owing to their reduced weight. Both processing and end use put special demands on the stabilizer package incorporated in the poly(propylene) resin phase of the GMT composite. A novel ternary antioxidant blend based upon an aromatic amine type stabilizer for superior processing stabilization in GMT will be presented. Processing stabilizer performance data, as measured by the critical weight loss test at 230 °C, will be discussed. Comparison of the arylamine based blend, which is phosphite-free, with a traditional phosphite-containing package of otherwise similar composition confirmed the superior performance of the former.

Background

A rapidly growing application for antioxidants is in glass mat reinforced thermoplastics (GMT) automotive applications. The average passenger vehicle made in Europe today contains about 3-4 kg of GMT derived parts (or its more recent variation long fiber reinforced thermoplastics). Examples for finished GMT parts include the front-end module, seat base and underbody trays. Typically, GMT contains 20—40% by weight glass in a poly(propylene) matrix, with the latter utilizing a carbon black load level ranging from 0.5—2% by wt. GMT is a demanding application area with regard to the necessary stabilization during processing and end use [1-3]. This is especially true of the processing step that typically proceeds at roughly 230 °C.

Blends of phenolic, phosphite and thioether stabilizers are often used in order to meet these stringent demands. However, in our hands, in order for GMT formulations containing traditional blends to provide sufficient processing stabilization, relatively high antioxidant load levels were necessary. A high antioxidant dosage, however, is undesirable since it may lead to bloom and thus delamination of the glass compound. Another factor resulting from increased antioxidant concentration is unfavorable economics. Against this background we report here on the development of an antioxidant package with superior performance compared to traditional phenolic/phosphite/thioether combinations. The rationale behind the novel antioxidant combination was to replace the phosphite component in traditional blends with an arylamine antioxidant, thus furnishing a phosphite-free package comprising arylamine, thioether and phenolic components [4].

Experimental

Molding of Poly(propylene) Films

0.5 mm thick poly(propylene) films were prepared using an Atofina 3882 type resin having a melt flow index MFI=100. All formulations contained 0.1% Calcium Stearate F (Crompton) and 1% Printex 60 carbon black (Degussa). After weighing in the additives, the dryblends were then mixed at 185 °C in a Brabender type 60 g mixing head for 15 min. The resultant product was used to compression-mold 0.5 mm 6 x 6 " films at 380F for four minutes. These were cut to size as needed.

Glass Mat Reinforced Poly(propylene)

An ecoMat® G-500 glass mat type product (Schuller, Germany), cut to approximately 6 x 3" in size, was sandwiched with two 6 x 3" poly(propylene) films. Two of these three-layered sandwiches were then combined by placing them back-to-back, resulting in a six-layered sandwich specimen whose approximate glass content was 30% by wt. The latter was then compression molded at 380F for three minutes. After allowing it cool, the composite product was placed in a circulating hot air oven at 230 °C for 90 s. The resultant GMT sheet was then used as-is in weight loss testing at both 230 °C and 150 °C.

Weight Loss Test on Glass-filled Compound

Weight loss testing was done by exposing GMT sheets in a circulating hot air oven (Blue M type) at the specified temperature. To determine processing stability, the samples were exposed at 230 °C. For long-term heat aging stability, the temperature was adjusted to 150 °C. After removing the test specimens they were cooled in a desiccator and then weighed. Duplicate samples were run.

Antioxidants

Antioxidants AO-1 (Naugard 445), P-1 (Naugard 524), S-1 (Naugard DSTDP) and AO-4 (Naugard 10) were all sourced from Crompton and used as is.

Results and Discussion

Commercial GMT compounds are molded in a tool maintained at room temperature (or slightly higher). Prior to the molding step, the GMT sheet is heated to 190–200 °C in an infrared oven. At this temperature it is critical for the antioxidant package to provide an adequate level of protection. Secondly, since the finished product will often be used in an automotive under-the-hood application, a sufficient quantity of active antioxidant is needed after the processing step to provide the necessary long-term heat stabilization.

Arylamine antioxidants have long since been known to act as superior primary antioxidants that are particularly useful in the stabilization of carbon-black containing thermoplastics like poly(propylene) [5-7]. Examples of commercially available arylamines include AO-1, AO-2 and AO-3 (Fig.1). We report here that when arylamine stabilizer AO-1 was combined with AO-4 and S-1 (at a weight ratio of 1:2:6 for AO-4:

AO-1: S-1), the resultant ternary blend T-1 gave superior processing stability compared to the control, as evidenced by measuring weight loss on the glass sheet at 230 °C. At the same time blend T-1 gave sufficient long-term heat aging stability, as determined by measuring weight retention at 150 °C. This testing was done relative to a control antioxidant package that consisted of AO-4 (phenolic component), P-1 (phosphite) and S-1 (thioether) (cf. Fig. 1). The AO-4: P-1: S-1 weight ratio was 1:2:6.

Both the control and ternary blend T-1 were formulated into poly(propylene) films that were subsequently used to make glass-filled compounds. After recording their unaged weight, appropriate test specimens were placed into a circulating hot air oven. One evaluation was performed at 230 °C (i. e. processing stability), the other at 150 °C (i. e. long-term heat aging). Results from weight loss testing are summarized in Table I. The data showed that arylamine-based blend T-1 gave much better processing stabilization than the traditional phosphite containing control. For example, a glass filled poly(propylene) sheet containing T-1 showed only 0.3% weight loss after 30 min. of aging at 230 °C. With the control package, by contrast, a similarly prepared glass-filled poly(propylene) sheet underwent catastrophic 16% weight loss. The data in Table I further showed that T-1 also provided slightly better long-term heat aging protection, as determined by measuring weight loss at the less stringent 150 °C.

At this point the rationale behind the weight loss test as a means to evaluate the stabilizer efficacy in glass mat reinforced thermoplastics shall be discussed. It has been suggested that measuring weight loss of the glass-filled product represents no more than tracking volatility of the antioxidant. However, this appears not to be the case as is evident from the degree of weight loss reported here. A case in point is the initial antioxidant dosage level of 1% relative to poly(propylene) weight. From this follows that any weight loss exceeding that value is caused by a factor other than additives volatility. We suggest here that the main reason for excessive weight loss is mechanical failure or disintegration of the system. In that sense measuring weight loss becomes rather meaningful for evaluating antioxidant activity. It should be noted that when in our hands weight loss exceeded roughly 2%, such disintegration became quite noticeable. This phenomenon will be further illustrated in the following discussion of the change in surface texture of glass-filled poly(propylene) during aging. The surface of an unaged material typically is fairly smooth and has a slightly glossy appearance to it. Individual glass fibers or strands from the glass mat are barely visible on the surface. During the oven aging process, once the weight loss percentage was greater than roughly 2%, the surface began to change its appearance quite dramatically. At that point individual glass fibers began to pop out with the result that they became visible and palpable. The test specimens simultaneously lost their initial glossy surface appearance. These observations corroborated mechanical failure as the cause for the weight loss occurring in the oven rather than additives volatilization. Hence measuring weight loss is a meaningful tool for comparing stabilizer activity in glass-filled thermoplastics. The better the retention of the initial weight, the more powerful is the antioxidant.

Above discussion may help clarify the role played by arylamine antioxidant AO-1 as one of the components in ternary blend T-1. The key compositional difference between the traditional AO-4/ P-1/ S-1 control blend and T-1 lies in the fact that in the latter arylamine AO-1 substituted phosphite P-1 in the former. (Although the ratio of arylamine to thioether to phenolic also played a role, as reported elsewhere [4], it was not until AO-1 was used instead of P-1 that weight retention improved dramatically). The superior high-temperature stabilization effect of arylamine vs. phosphite antioxidant may be rationalized as follows. Firstly, arylamine antioxidants can engage in a multitude of radical chain-inhibiting reactive pathways [5]. Secondly, it is possible that either the glass or carbon black surface, or both, compromised the activity of the phosphite (by e. g. hydrolysis or adsorptive immobilization). Lastly, it is also possible that the phenomenon of T-1's superior performance falls within the realm of synergy between the three blend components AO-1, S-1 and AO-4.

Conclusions

Glass mat reinforced poly(propylene) sheets are made by high-temperature flow molding. To mimic the demands on the antioxidant during the processing step, a weight loss test has been devised. The traditional phenolic/ phosphite/ thioether antioxidant combination gave premature mechanical failure in the glass-filled system. When the arylamine antioxidant substituted the phosphite to give a three-component blend of arylamine/ thioether/ phenolic, initial weight retention of the test specimen improved dramatically. The weight loss test in itself was identified as a meaningful way to evaluate and compare different antioxidants. The percentage weight loss observed during testing was found to exceed the value expected for plain additives volatilization. Rather, it tracked mechanical failure of the system.

References

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Keywords

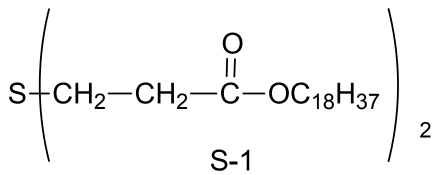
Glass mat reinforced thermoplastics, aryl amine antioxidant, phosphite, carbon black, 4,4'-Bis(α,α-dimethylbenzyl)diphenylamine

*Table I: Comparison of processing stability and long-term heat aging data.**

Antioxidant (at 1% conc. relative to PP)	**Wt. Loss (%) after 30 min. at 230 °C**	**Wt. Loss (%) after 28 days at 150 °C**
Control	16	10
T-1	0.3	9

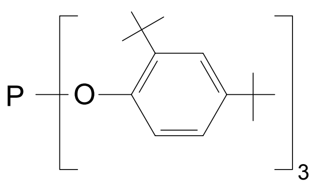
∗*Testing done on glass mat reinforced poly(propylene) test specimens prepared as described under Experimental.* ***Control****: AO-4: P-1: S-1 = 1:2:6.* ***T-1****: AO-4: AO-1: S-1 = 1:2:6*

Figure 1: Antioxidant Structures



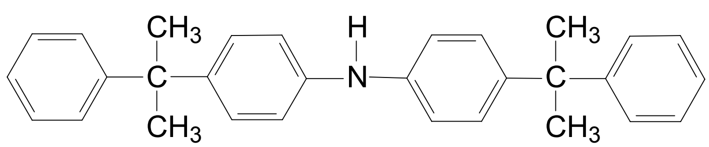
S-1

Distearylthiodipropionate



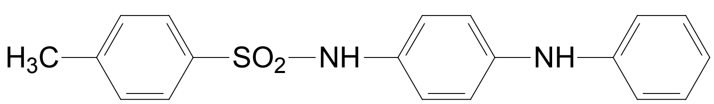
P-1

Tris-(2, 4-di-t-butylphenyl)phosphite



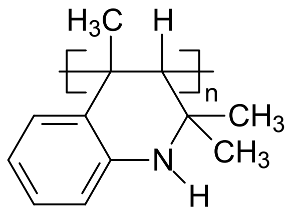
AO-1

4,4'-Bis(alpha, alpha-dimethylbenzyl) diphenylamine



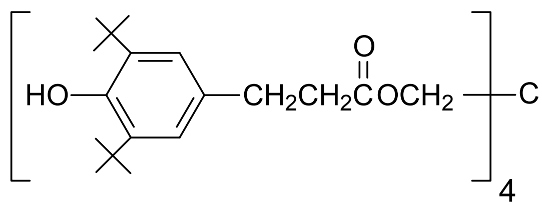
AO-2

p-(p-toluene-sulfonylamido)- diphenylamine



AO-3

Polymerized 1,2-dihydro-2,2,4- trimethylquinoline



AO-4

Tetrakis[methylene(3,5-di-t-butyl-4- hydroxyhydrocinnamate)]methane