

Talc-filled PP: A new concept to maintain long term heat stability

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Received 4 August 2006; received in revised form 1 September 2006; accepted 1 September 2006

Available online 17 October 2006

Abstract

Talc as filler improves the mechanical properties of polypropylene. However, talc also reduces the efficiency of many stabilizers and so the life-time of a final product.

In a study to find new modifiers to improve the heat stability of talc-filled PP formulations it was observed that selected blends of modifiers were more efficient than the single modifiers at the same total loading.

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Keywords: Ageing; Amphiphiles; Fillers; Talc; Poly(propylene) (PP); Stabilization

1. Introduction

Talc is the most important filler for polypropylene. It improves heat deflection temperature (HDT) and stiffness (Young's modulus) [1]. Talc nucleates PP and so reduces cycle time in moulding applications, thermal expansion coefficient (CLTE), and gas permeation rate.

But talc can also adsorb stabilizers on its surface and so reduces the service life-time of the products [2,3]. This adverse effect can be reduced or prevented by adding more stabilizers to compensate for the adsorbed part, or by adding modifiers with higher affinity for talc to coat the talc surface. Oligomeric epoxy resins [4], polypropylenes grafted with maleic anhydride [5] or acrylic acid [6] are frequently used for this purpose.

If a stabilizer has a high affinity to the talc surface it will be adsorbed until the talc surface is covered. The polymer matrix would remain almost free of stabilizers, and at this point you would observe the largest difference between a formulation with or without talc, or a formulation with a well deactivated talc surface (Fig. 1). Filler surface deactivation is most

rewarding at high filler loadings and medium heat stability requirements.

A convenient way to study talc-to-additive interactions is to stir an additive solution over suspended talc. Talc is filtered off and the additive concentration of the filtrate is determined [3,7]. This simple technique gives fast results, but possible interactions among additives and volatility of low molecular mass compounds could be overlooked.

It was decided to compound all formulations on a twin-screw extruder, to injection mould plaques and to test their heat stability in ovens at elevated temperature.

2. Experimental part

PP (80%), AO-1 (wt% based on PP resin), 0.1 phr PS-1, 20% talc T-1, and modifiers M (wt% based on total formulation) were dry-blended in a Henschel mixer, compounded on a 25 mm twin-screw extruder with $L/D = 46$ from Berstorff at 230 °C and injection moulded on a Engel K70 at 240 °C to 2 mm tensile impact bars. The bars were exposed in ovens at 135 and 150 °C till first signs of degradation. The days till degradation were recorded.

PP-1: Profax PH 350, PP-2: Moplen HF 500 N; both PP homopolymers were supplied by Basell.

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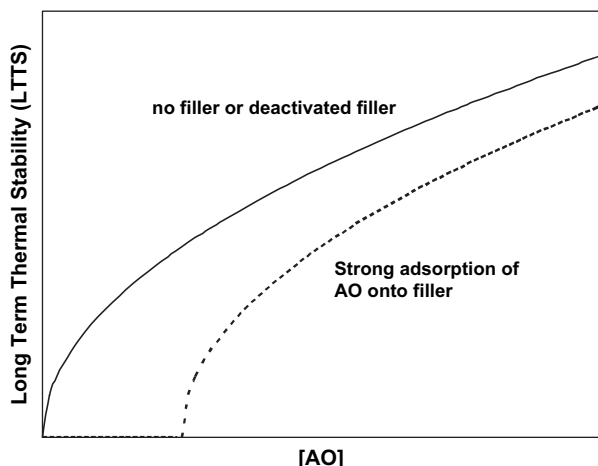


Fig. 1. Oven ageing as function of the AO concentration.

T-1: Luzenac® A-20, T-2: Luzenac® OOS; both talc grades were supplied by Luzenac.

AO-1: pentaerythritol tetrakis [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate] (Irganox® 1010).

PS-1: tris(2,4-di-*t*-butylphenyl) phosphite (Irgafos® 168).

TS-1: dioctadecyl 3,3'-thiodipropionate (Irganox® PS 802).

M-1: ethylene bisstearylamine (Atmer® SA 1760).

M-2: oligomeric acrylester (Irgastab® CA 100).

M-3: stearyl sorbitane (Atmer® 103).

M-4: glycerol monostearate (Atmer® 129).

M-5: ethoxylated alkylamine (Atmer® 163).

M-6: ethoxylated alkylamide (Atmer® 167).

M-7: oxidized PE-HD (A-C® 395), supplied by Honeywell.

M-8: poly(ethylene-*co*-vinyl acetate) (A-C® 400), supplied by Honeywell.

M-9: poly(ethylene-*co*-acrylic acid) (A-C® 540), supplied by Honeywell.

M-10: polyethyleneglycol 1000, supplied by Fluka.

M-11: polyvinylalcohol (Erkol® V03/300), supplied by Celanese Corp.

M-12: dodeceny succinic anhydride, supplied by Fluka.

3. Results and discussion

First we checked the influence of the processing conditions on the heat stability of the formulations. A formulation containing 0.4 phr AO-1, 0.2 phr TS-1, 20% T-1 and 0.2% M-1, together with two reference formulations, was processed using different feeding conditions:

Ref: is a reference formulation without talc but with modifier.

No modifier: is a reference formulation with talc but without modifier.

D1: with talc fed separately in the side-feeder,

D2: polymer with stabilizers, talc, and the modifier was blended and dosed as powder blend in the hopper,

D3: polymer with stabilizer and modifier was compounded and dosed as pellets with talc fed separately in the hopper, or

D4: polymer with stabilizer was compounded and dosed as pellets with a blend of talc and modifier fed separately in the hopper.

Half of the granules were extruded a second time and first and second extrusions were injection moulded to 2 mm impact bars. The bars were exposed to draft ovens at 135 and 150 °C until first signs of degradation were visible.

The heat stabilities of the samples were quite similar, all formulations containing talc and modifier degraded after approximately 65 days at 150 °C, independent of the processing conditions (Fig. 2). The second extrusion cycle led to a small reduction of the life-time of the samples. The formulation with talc added by the side-feeder was slightly more heat stable than the remaining talc containing formulations.

The reference formulation (no modifier) (with the same stabilizer package) with talc but without modifier degraded after about 30 days at 150 °C, and the talc-free reference (Ref) outperformed the remaining samples (about 90 days at 150 °C). The formulation without talc and without modifier failed after 120 days.

The slight (not significant) decrease of the heat stability after two extrusion passes could be explained either with higher stabilizer consumption due to the second extrusion step or with a higher talc surface due to additional shear or some degradation of the stabilizer. The better oven stability of formulation (D1) where talc was fed by side-feeder to the melt, might be due to less shearing of the talc and hence smaller surface area of the talc.

To see whether the lengthy oven ageing test could be avoided and substituted by measuring the oxygen induction time (OIT), the same samples were heated to 200 °C, and after switching to oxygen the time to onset of the exotherm was determined. The formulations with talc and modifier gave OIT values of 70–90 min, independent of the processing

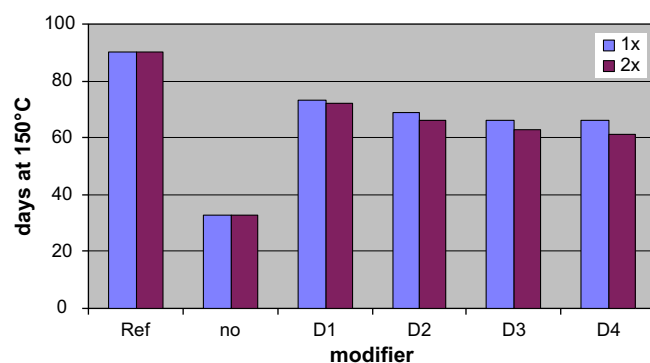


Fig. 2. Long term heat stability in function of feeding conditions: 80% PP-1 (with 0.4 phr AO-1 and 0.2 phr TS-1) with 20% T-1 and 0.2% M-1; twin-screw extruder at 230 °C, injection moulded at 240 °C, 2 mm plaques; 1×, 2×: extrusion cycles; D1: PP pellets in hopper, talc by side-feeder, D2: powder blend in hopper, D3: PP pellets with modifier + talc in hopper, D4: PP pellets + talc with modifier in hopper, Ref: no talc.

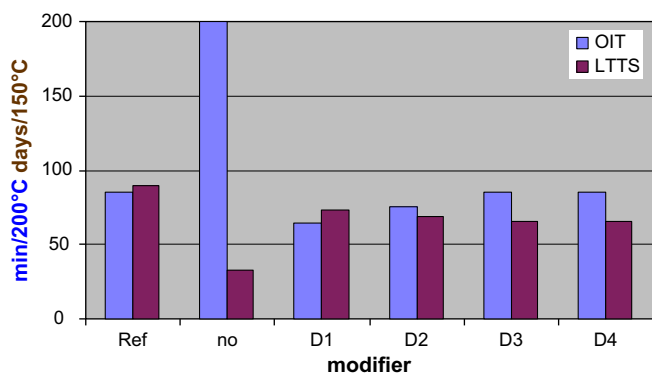


Fig. 3. Heat stability by oven ageing vs OIT. LTTS: days to initial decomposition in oven ageing at 150 °C, OIT: oxygen induction time at 200 °C. See also legend of Fig. 2.

conditions. The reference without talc, the most heat stable formulation in the oven test, oxidized after 90 min, but the reference with talc but no modifier, the least stable formulation in oven ageing, degraded after 200 min (Fig. 3).

The results showed no correlation between OIT and oven ageing. The surprising discrepancy between OIT and oven ageing results of the modifier free talc formulation could be explained that the uncoated/unmodified talc surface may degrade AO-1 to more OIT active decomposition products, e.g. by hydrolysis of the ester group or debutylation of the phenolic moieties.

In the succeeding tests several modifiers were checked for their effects on the heat stability of the PP/talc formulations. Three amphiphilic coupling agents with similar molecular masses were selected, all with a hydrophilic end to bind onto the talc surface and the hydrophobic tail to prevent adsorption of stabilizers and to maximize interactions with the polymer matrix. The hydrophilic part of the molecules was composed of two hydroxyl groups and a further polar moiety, an ester group (M-4), an amino group (M-5), or an amido group (M-6) (Fig. 4).

Despite the similarities of the chemical structures of M-4 to M-6 large differences in the oven ageing test were observed. M-6 with the amido group performed best, followed by M-4 with the ester group, and M-5 with the amino group was inferior but still improved the heat stability of the formulation. The results are shown in Fig. 5.

Further modifiers were tested (formulations based on 0.1 phr AO-1, 20% T-1 and 0.2% modifier M). The good performance of M-1, a bisamide, confirmed the above findings (Fig. 6).

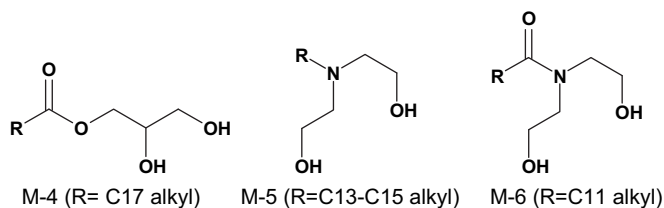


Fig. 4. Structure of amphiphilic compounds.

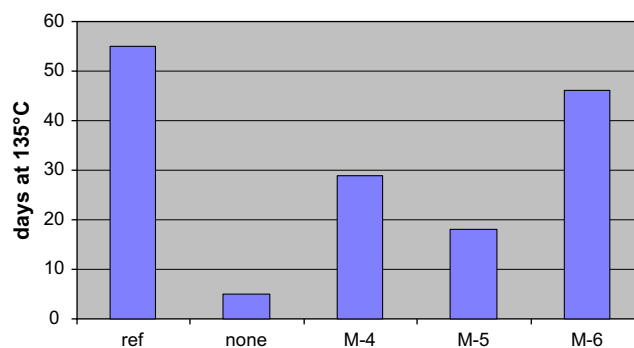


Fig. 5. Effect of amphiphilic modifiers on the stability of talc formulations. PP-1 (79%) with 0.05 phr AO-1, 20% T-2 and 1% modifier; Ref: PP-1 with 0.05 phr AO-1.

Surprisingly, it was observed that large improvements could be found when blends of modifiers were used. Combinations of bisamide M-1 and the oligomeric acrylate M-2 at a total loading of 0.2 wt% (1 wt% based on talc) were able to recover more than 90% of the heat stability of the talc-free formulation, unlike the single components which regained 50 resp about 70% of the heat stability (Fig. 7).

Further combinations were tested and the results demonstrated that the observed synergism was valid for other blends (Fig. 8).

The rationales behind this synergism have not been elucidated. Assuming that the tested modifiers do not act as stabilizers (M-1 did not increase the life-time of a talc-free PP formulation) and the talc surface was not saturated (a 25% reduction of the modifier M-1 concentration led to a 20% reduced oven life-time), then the synergism must be based on preventing more efficiently the adsorption of the phenolic stabilizer onto the talc surface. The following hypothesis were considered:

- (1) After the initial results with the oligomeric acrylate it was speculated that the amphiphilic moiety improves the solubility of the oligomeric acrylate in the PP melt to allow a denser packing of the acrylate onto the talc surface or that the low M_w compound fills gaps left free by the oligomeric acrylate. But the effect was also observed with low

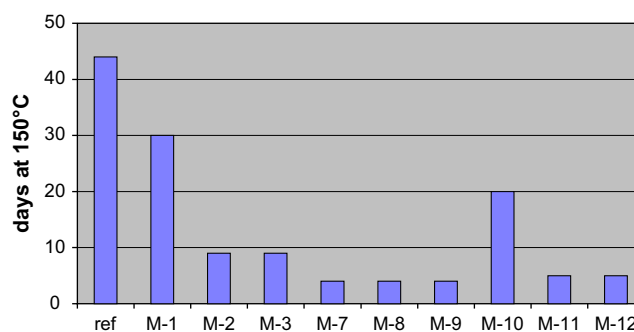


Fig. 6. Heat ageing improvements of different coupling agents. PP-2 (80%) with 0.1 phr AO-1, 20% T-1 and 0.2% modifier M; Ref: PP-2 with 0.1 phr AO-1.

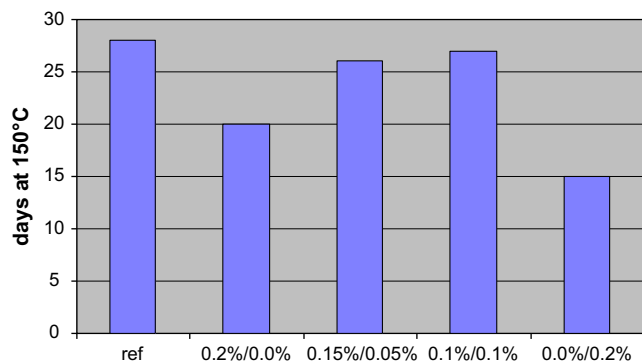


Fig. 7. Synergistic combination M-1/M-2. PP-1 (80%) with 0.1 phr AO-1, 20% T-1 and 0.2% (M-1 + M-2); Ref: PP-1 with 0.1 phr AO-1.

M_w products like M-1 combined with anhydride M-12 or sorbitane M-7.

- (2) Stabilizers with molecular masses below 500 Da are known to be inefficient at oven ageing temperatures of 150 °C due to their volatility. An improvement of the oven life-time of blends would be expected if the volatility of the talc coating modifier was reduced, e.g. by forming dimers or agglomerates by hydrogen bridges.
- (3) Generally a crystal has more than one crystal surface. If the adsorption sequence on the crystal surface (1) would be modifier A > stabilizer S > modifier B, and on surface (2) modifier B > stabilizer S > modifier A, than modifiers A and B could form a synergistic combination for stabilizer S.

4. Conclusions

The detrimental effect of talc on the heat stability of polypropylene can efficiently be reduced using synergistic blends

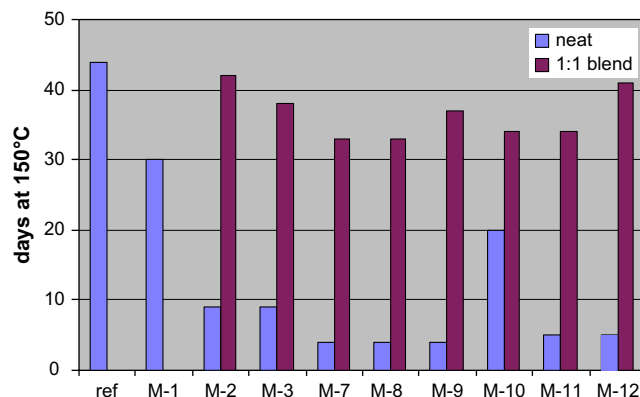


Fig. 8. Other synergistic combinations with modifier M-1. PP-2 (80%) with 0.1 phr AO-1 and 20% T-1; neat: 0.2% modifier M; blend: 0.1% M-1 + 0.1% modifier M; Ref: PP-2 with 0.1 phr AO-1.

of modifiers. The roots of the observed synergism are not understood and need further investigations.

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