

Evaluations of several halogen-free flame retarded Polypropylene formulations

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Förord

Denna studie är gjord av PP Polymer AB på uppdrag av Räddningsverket som via oberoende forskare ville ta reda på om plaster kan tillverkas med bättre brandegenskaper utan att göra avkall på andra kvalitéer. Det är ett led i arbetet med att minska behovet av ifrågasatta flamskyddsmedel.

Det tvådelade projektet genomfördes för att ta reda på hur brandegenskaperna för en vanlig polymer kan påverkas med olika tillsatser. Kunskap om detta kan visa på vägar att förbättra dessa egenskaper. Den första studien beskriver viktiga parametrar som påverkar brännbarheten hos polymeriska material och olika metoder för att förbättra brandegenskaper för dessa material summerades. Effekten av flamskyddsmedlen är beroende av de olika typerna av polymerer och deras nedbrytning bör detta beaktas vid val av testmetoder. Utöver dessa brandrelaterade egenskaper måste tillsatsernas inverkan på själva polymerens egenskaper bedömas. För att undersöka hur flamskyddet åstadkoms testades ett par kommersiella polymerer. Analysresultat visar att additiven bara används för att påverka den termiska stabiliteten och effekten bedömdes som marginell. Nyttan och användbarheten av dessa additiver ifrågasattes även om materialet klarar de krav som ställs vid brandtester.

I studien föreslogs ett fortsatt utvecklingsarbete med inriktningen att minska koncentrationen av flamskyddsmedel genom att också utnyttja andra flamskyddsmekanismer. Vid upphandlingen av projektet överenskomms med PP Polymer AB att företaget äger alla rättigheter till recepten så därför anges här enbart de huvudsakliga ingredienserna.

Vid andra delen av studies har tillsatser till polypropylen studerats och den visar att flera mekanismer kan utnyttjas. Resultatet förutsades i den första studien. Liknande resultat kan troligen åstadkommas även för andra polymerer. För framtiden önskar vi provmetoder som även kan redovisa och jämföra polymerernas brandsäkerhet. Idag saknas ofta drivkrafter för att förbättra dessa egenskaper eftersom det räcker med att redovisa att testernas kravnivåer har uppfyllts.

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Sammanfattning

En utvärdering av ett flertal blandningar visar att det är möjligt att göra helt halogenfri och flamskyddsbehandlad polypropylen baserade system utan att påverka vare sig tillverkningsprocessen eller materialets egenskaper.

Studien visar att det bästa sättet för att nå maximala brandskyddsegenskaper är att kombinera flera mekanismer genom att välja lämpliga tillsatser. Den huvudsakliga invändningen som förs fram emot halogenfria alternativ är att de bara fungerar vid höga koncentrationer vilket är till nackdel vid tillverkningen och påverkar materialets egenskaper.

Här visas att dessa nackdelar kan undvikas genom att använda tillsatser som har flera effekter. I denna rapport presenteras flera helt nya blandningar som visar mycket goda flamskyddande egenskaper utan att påverka materialet. Eftersom blandningarna består av olika kommersiellt tillgängliga tillsatser och används i måttliga mängder så kommer troligen inte priset att bli högre än med dagens alternativ.

Vi har i undersökningen inte försökt att optimera någon av blandningarna förutom de som haft inverkan på flamskyddets mekanismer. Det har visats att dessa nya blandningar fungerar i praktiken.

Abstract

Evaluation of several formulations in this report reveals that it is possible to formulate absolutely halogen free flame retarded polypropylene based systems without affecting either the processing and the properties of the material.

The study shows that the best way to achieve the maximum fire-retardant properties is to combine several of the fire retarding mechanisms by selecting suitable additives. The main restriction, which has been put forward against the halogen-free additives, is that they function at high loadings, that in turn influences both the processing and the properties of the materials.

In this it has been shown that this limitation can be avoided by using additives having combined mechanisms. In this report, we have presented several novel formulations that show very good fire retardant properties without affecting the material. Since, the formulations comprise of several commercially available additives at rather low loadings, the formulations are not expected to have high price compared to the present alternatives.

In this investigation no attempt has been made to optimise any of the formulations except formulations based on different fire retarding mechanisms have been evaluated and it has been verified that such systems functions in practice.

Introduction

In our earlier state-of-art study of flame retardancy of polymeric materials (report 2001-06-30), we reviewed basic fire mechanisms and how to control them. It was suggested that the easiest way to control the fire retardancy is by adding suitable additives to the polymeric material. Such additives mainly functions either by controlling the gas-phase or condensed phase reactions or both. So far the condensed phase reactions are concerned, additives are mainly used either to increase thermal stability of the polymers, or to increase the char formation as a result of burning or to decrease the diffusion of combustible gases from the material to fire formed as a result of thermal degradation or finally to reduce heat transfer from fire to material. Additives that form radical quenchers as a result of fire stop exothermic chain reactions in the gas-phase and thereby mainly control the gas-phase reactions.

Flame retardancy can also be obtained by physically influencing the polymers on fire. The various physical phenomenon that are used for such purposes are e.g. dilution and sink effects of the combustible gases formed as a result of burning, endothermic decomposition of the additives or finally formation of impermeable surface skin that can prevent diffusion of combustible gases to the flame and insulate the surface from heat flow from the flame to the polymer.

While selecting suitable flame retarding (FR) additives it is essential that they function as effective flame-retardants and at the same time do not affect the mechanical and processing properties of the polymers. In our earlier study, we also reviewed different measuring

techniques to measure the fire properties of polymers and how to determine the effectivity of the FR additives. Based on the literature survey, it was suggested that thermo-gravimetric analysis (TGA) and Cone-calorimeter are most suitable measuring techniques.

In this investigation we present our results on the evaluation of various halogen-free FR additives mainly for the polypropylene (PP) material, where we have for the first time combined several fire retarding mechanisms. Most of the halogen free formulations reported earlier were based on one additive, which meant that rather large amounts of additives were required to obtain the required effect. The latter resulted into both processing problems and also the properties of the final product were not up to full satisfaction. In order to show that these additive combinations do not influence the physical and processing properties of the polymer compounds in a negative way, we also measured such properties. We selected PP, as base material for our investigation; due to the fact that it is used in large quantities in different industrial applications where they are fire retarded by using halogen based FR additives.

Experimental

We have evaluated 18 different additive formulations and due to proprietary reasons we cannot disclose any of these formulations in this report instead we have referred these formulations as FR PP/ 1 to FR PP/18. For our compounds we used a commercial quality of PP and all the experimental results were compared with the virgin PP material and commercially flame retarded PP grade containing brominated and halogen free FR additive referred as reference material 1 and 2 in this report. In our formulations we have used combination of additives belonging to the family, N-P compounds, red phosphorus, expandable graphite, conventional aluminium trihydrate (ATH) and magnesium hydroxide, molybdates, borates, organo-clays etc. in different concentrations.

All the compounds were prepared by melt blending in a Brabender mixer at a temperature of 170°C for 35 min.

All the compounds were then characterized for rheological, thermal, and mechanical properties. Density for all the compounds was also measured. Rheological properties were determined by measuring melt flow index (MFI) according to ISO 1133 standard.

All the mechanical testing was performed on thin sheet samples with dimension: 70 mm long, 10 mm wide and 0.1 mm thick on a tensile tester at a drawing rate of 1 mm/min according to ASTM D882 standard.

Density of all the compounds was determined according to IEC 811 standard. Thermal degradation behaviour was measured by TGA 850 instrument supplied by Mettler-Toledo. They were measured both under the isothermal and adiabatic conditions. For isothermal measurements we found 250°C was a suitable measuring temperature based on the degradation rate. For adiabatic conditions we ran the samples in the temperature range 50-800 °C.

Heat deformation temperature for all the PP compounds was measured by using Thermal Mechanical Analysis (TMA) at a static stress of 0.5 N.

Viscoelastic properties were measured by using Dynamic Mechanical Analysis (DMA) in the extension mode at 1 Hz frequency between -80 and +140°C.

Results

a) Melt Flow Index (MFI)

Melt flow index (MFI) values for all the compounds can be summarized as below:

Sample	MFI (g/10 min)
Flame retarded, ref 1	11 – 21 (from material data sheet)
Flame retarded, ref 2	5,7
Virgin PP	2.0
FR PP/ 1	16.4
FR PP/ 2	24.5
FR PP/ 3	22.5
FR PP/ 4	18.6
FR PP/ 5	28.5
FR PP/ 6	21.5
FR PP/ 7	16.2
FR PP/ 8	21.5
FR PP/ 9	27.5
FR PP/ 10	23.2
FR PP/ 11	18.8
FR PP/ 12	11.1
FR PP/ 13	10.0
FR PP/ 14	10.5
FR PP/ 15	21.0
FR PP/ 16	20.5
FR PP/ 17	17.3
FR PP/ 18	32.5

High value of MFI means that the material is easy to flow and is thereby easy to process. Quite often low MFI values create form-filling problems and are therefore not desirable from the processing point of view.

Comparison of the rheological properties of the new formulations with the virgin material and also with the reference materials reveal that the presence of additives has not caused any deteriorating influence on the processing properties of the materials except formulation FR PP/18, which shows rather high value.

b) Physical Properties

Tensile modulus and %-elongation at break results can be summarized as below:

Sample	Tensile modulus (N/mm²)	%-elongation
Virgin PP	22.7	6.4
FR PP/ 1	22.1	5.6
FR PP/ 2	21.4	3.6
FR PP/ 3	15.9	2.7
FR PP/ 4	21.0	4.6
FR PP/ 5	21.5	4.2
FR PP/ 6	20.2	5.5
FR PP/ 7	16.1	2.5
FR PP/ 8	14.7	2.6
FR PP/ 9	17.2	3.2
FR PP/ 10	20.0	8.0
FR PP/ 11	Samples could not be prepared	
FR PP/ 12	14.6	4.1
FR PP/ 13	22.3	4.8
FR PP/ 14	20.1	4.5
FR PP/ 15	21.5	6.5
FR PP/ 16	20.2	7.0
FR PP/ 17	20.5	6.5
FR PP/ 18	19.0	4.5

The results show that mechanical properties are also not affected to any significant levels due to the presence of these FR additives. As is mentioned in the table, it was however difficult to prepare samples from compound FR PP/11.

Char contents, densities and heat distortion temperature (HDT) values of different PP samples are summarized below:

Sample no.	Density (g/cm³)	HDT (oC)	Char content (%)
FR ref 1	1.325	-	19-23 (from data sheet)
FR ref 2	0.900	-	0
Virgin PP	0,905	153.4	0
FR PP/ 1	1.139	158.8	19.36
FR PP/ 2	1.146	151.6	19.41
FR PP/ 3	1.130	157.0	20.20
FR PP/ 4	1.036	154.1	18.06
FR PP/ 5	1.055	152.9	16.35
FR PP/ 6	1.071	152.4	16.77
FR PP/ 7	1.091	152.1	17.84
FR PP/ 8	1.102	151.6	16.93
FR PP/ 9	1.082	147.2	19.56
FR PP/ 10	1.093	152.8	13.41
FR PP/ 11	0.887	149.3	22.77
FR PP/ 12	1.031	152.1	21.00
FR PP/ 13	1.036	150.9	15.97
FR PP/ 14	1.035	153.4	16.91
FR PP/ 15	1.045	154.6	12.70
FR PP/ 16	1.025	151.1	11.03
FR PP/ 17	1.023	152.4	11.64
FR PP/ 18	0.989	154.3	9.66

Results show that addition of halogen free additives have not resulted in any increase in density although char contents in the formulations have increased substantially. Moreover, comparison with the reference sample shows that the increase in densities in our formulations is very low compared to ref 1, which is presumed to be flame retarded by some type of inorganic FR additive. HDT values are also not affected in our new formulations compared to the virgin material.

c) Heat stability (TGA)

In order to investigate the thermal stability behaviour of these novel formulations and in order to compare the results with the virgin and the reference flame retarded materials we analysed these samples by TGA both under isothermal and adiabatic conditions.

In order to select a suitable temperature for isothermal runs, we performed isothermal measurements at 200 and 250°C as a function of time. We were interested here to find a temperature that showed a reasonable degradation rate for the PP samples. We analysed virgin (PP 0) and PP 1 sample at these temperatures and the results are shown in figures 1 and 2.

Figures show that the degradation rate is rather low at 200°C for the flame retarded sample and therefore we selected 250°C as the suitable temperature for all our further studies.

Rate of thermal degradation under isothermal conditions at 250°C for 200 min for all the PP compounds are summarized in figures 3-5. Figure 6 summarizes the isothermal results for the unmodified PP (PP 0) and two commercially available flame-retarded PP qualities (FR Ref 1 and 2). The results show varying degrees of thermal stabilities for different formulations. Several of our novel formulations show very good thermal stabilities compared to the unmodified sample.

To investigate differences in the thermal stabilities of different samples, we also measured %-weight loss as a function of temperature between 50-800°C. A summary of the %-weight loss at 300 and 350°C is shown in figures 7 and 8.

Figure 7

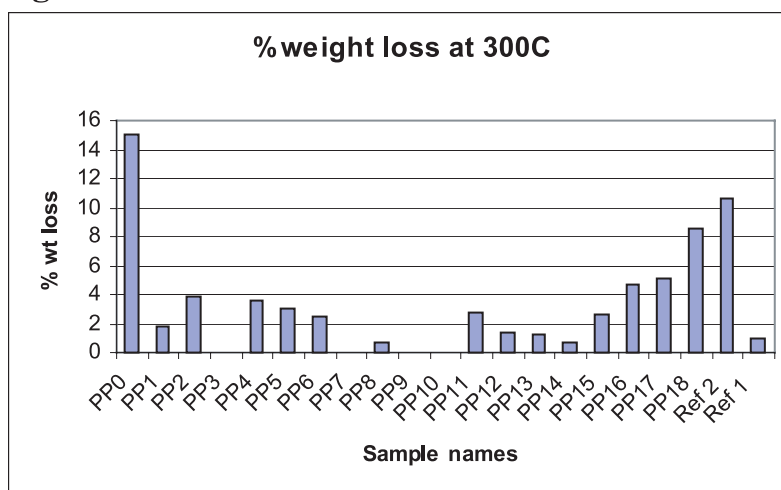
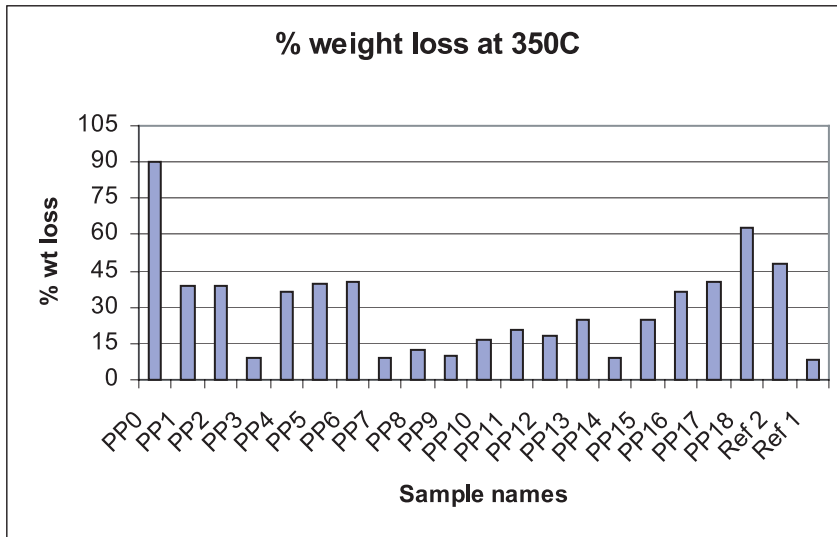


Figure 8



Results show that the new formulations PP 3, 7, 8, 9 and 14 have very low weight losses both at 300 and 350°C compared to the unmodified PP, which shows 15 and 90% weight losses at these temperatures.

From these measurements we also determined temperatures corresponding to 30 and 50% weight losses for the various formulations and the results are summarized in figures 9 and 10 below.

Figure 9

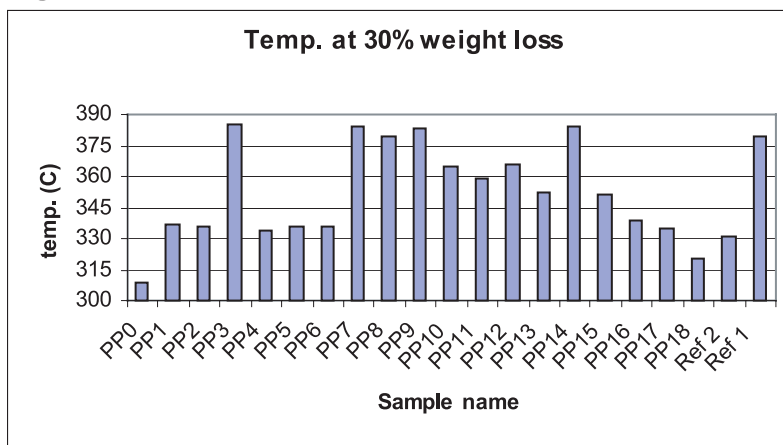
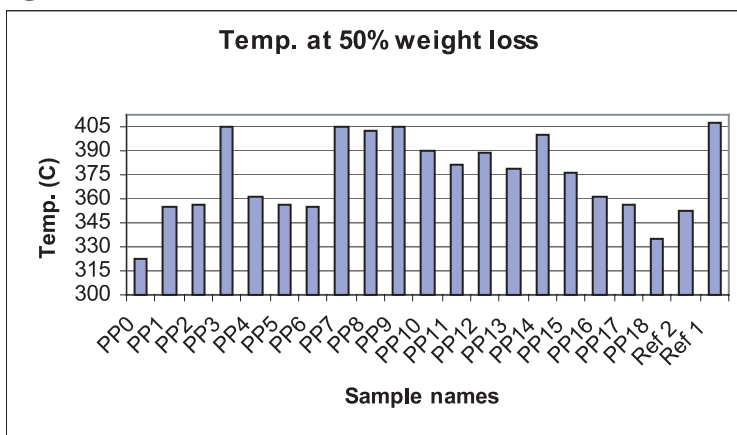


Figure 10



The results show that unmodified PP exhibits 30 and 50% weight loss at 308 and 322°C respectively whereas the formulations mentioned as above show temperatures >380 and 400°C. These degradation temperatures are also higher than the commercial samples.

Full range degradation behaviour of all our new compounds and for the unmodified PP together with the reference flame retarded materials are shown in figures 11 and 12.

d) Viscoelastic properties (DMA)

DMA is used to measure viscoelastic properties of the polymeric materials. Viscoelastic properties of polymeric materials are a measure of the fraction of elastic component (E') and fraction of viscous component (E''). Elastic component arises from the elastic deformation of the chains arising from the amorphous and the crystalline part of the material whereas the viscous part arises from the movement of polymer segments.

In DMA measurement, a prestressed polymer sample is exposed to a sinusoidal stress and the sinusoidal strain formed as a result of this stress is measured. From the measurements of maximum stress, maximum strain and the phase difference between the sinusoidal stress and strain, E' and E'' as a function of temperature can be determined. From these values, $\tan \delta$ values, as a function of temperature ($\tan \delta = E'' / E'$), can also be determined. Peak $\tan \delta$ -values represents glass transition temperature, T_g for a specific material at a defined frequency. In general, T_g determined by DMA does not correspond to the values determined by DSC because in case of DMA, segmental motions of the polymer chains affect T_g .

Both the E' and $\tan \delta$ -values for all the new formulations and unmodified PP are shown in figures 13-18. As evident from the figures, the viscoelastic properties of the base material are not much affected by the new flame retardant additive combinations.