

Evaluation and Characterization of Ammoniumpolyphosphate–Pentaerythritol-Based Systems for Intumescent Coatings

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ABSTRACT: Intumescent coatings are increasingly used as a method of passive fire protection on steel constructions. By forming a carbon network and releasing a blowing agent, the thin intumescent film swells 100-fold at elevated temperatures. The highly insulating foam effectively prevents the load bearing steel from reaching its critical temperature at which it loses its mechanical properties and collapses. The role of the carbon donor in intumescent coatings has been studied. Comparison in temperature development, foaming ratios, and rheological behavior has been performed between formulations containing pentaerythritol (penta), di-penta, and tri-penta. A simulated fire test, in which the temperature development during intumescence was studied, showed that the formulations containing penta

were considerably more efficient in keeping a low temperature throughout the process. A more rapid temperature development was displayed when using di-penta and tri-penta as the carbon donor. Rheometer tests indicate that penta formulations enter the intumescent process at a lower temperature and stays in it for a longer time than di-penta and tri-penta formulations. Furthermore, the crossover temperature and maximum phase angle are shifted towards higher temperatures by replacing penta with di-penta and with tri-penta in the formulations, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 748–753, 2007

Key words: intumescence; rheology; flame retardancy; foam extrusion

INTRODUCTION

Intumescent coatings have had a large increase in use, as a method of passive fire protection, over the past few years. Their main purpose is to protect construction materials such as steel and wood, in case of fire. Intumescent coatings are passive fire protections that swell when subjected to high temperatures. They also release nonflammable gases, such as H₂O, NH₃, and CO₂, which dilute the fuel gases and cool the surroundings by having high values of heat of gasification. Furthermore, the reactions taking place during intumescence are endothermic, contributing to absorb heat and prevent fire.^{1,2} By coating steel constructions with intumescent coating, the time increases before the steel reaches its critical temperature and collapses.¹ The main driving force for developing this type of fire protection has been to decrease the use of halogenated fire retardants as they are believed to be harmful for the environment.³ Furthermore, there is an increase in the use of steel constructions in architectural work. The success of intumescent coatings is their ability to develop a highly insulating layer of

carbon foam covering the steel when temperature surpasses a certain limit. Intumescent coatings need four main components with specific properties to function as a fire protector. An acid donor (ammonium polyphosphate, APP) is used to provide the system with acid, which can react with a carbon donor (pentaerythritol, penta). This reaction, which is an alcoholysis of APP (Fig. 1), is thought to determine the rate and efficiency of intumescence. The formed phosphor ester can undergo a ring closing esterification (Fig. 2), in which water and ammonia is released.⁴ A succession of these and similar reactions results in a char consisting of mainly carbon, but also small amounts of oxygen, phosphorus, and nitrogen atoms.⁵ When the temperature is raised, a simultaneous reaction takes place in which the blowing agent (melamine) releases nonflammable volatiles into the system (Fig. 3), causing the carbon network to swell to a thickness many times larger than the original thickness.^{6,7} The binder poly(vinyl acetate) not only functions as a component to bind the additives together, but it also has an effect on the intumescence since it is known to react with the acid donor. Furthermore, the binder takes part in the control of the char expansion and ensures a uniform foam structure.⁸

It has been previously shown that penta is an effective carbon donor for intumescent systems.⁹ However, the mechanisms of intumescence are relatively unknown and the role of the different components

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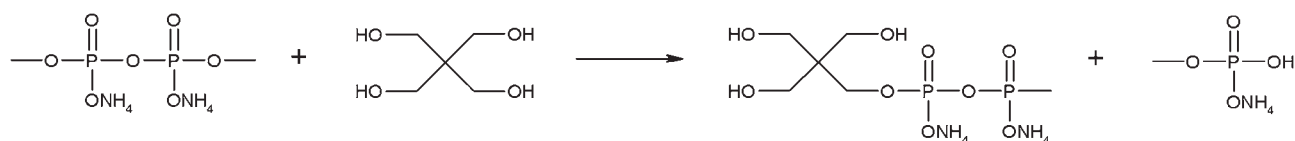


Figure 1 Alcoholysis of ammonium polyphosphate.

and what processes they control are not fully understood. In this work, the influence of the carbon donor in intumescent systems on the temperature development and rheological behavior of the formulations containing different carbon donors has been studied.

EXPERIMENTAL

Materials

Following chemicals were used in this study. Exolit AP 422 (Clariant), Charmor PM15, Charmor DP15 and tri-pentaerythritol (tri-penta) (Perstorp AB), melamine (DSM), Mowilith DM 230 (Celanese), titanium dioxide Kronos 2190 (Kronos), Natrosol 250 HR (Hercules-Aqualon) diluted to 2 wt % in water, sodium hexametaphosphate (Sigma-Aldrich), Aerosil 200 (Degussa), and butylglycol (Sigma-Aldrich). All chemicals were used as supplied.

Preparation of formulations

The formulations were prepared using a dissolver, DISPERMAT from VMA-Getzmann GMBH. The formulations are listed in Table I.

When the carbon source was varied in the formulation, the ratio between hydroxyl groups on the carbon donor and the active sites on the ammonium polyphosphate (APP) was taken into account so that the same amount of hydroxyl groups were added to each formulation. This was done to retain the ratio between hydroxyl groups and APP sites thus not changing the ratio between the reactants in the important alcoholysis in Figure 1.

Application of coatings

The coatings were applied on steel panels, with the dimensions 150 mm × 70 mm × 3 mm, with the use of a wooden spatula. The amount of dry content on each plate was constant, so that the added mass was

adjusted according to the dry content of the specific formulation.

Temperature development

The coated-steel panels were dried at room temperature during three days and subsequently tested in a simulated fire. A Bunsen burner was used at a constant gas flow as the heat source, as shown in Figure 4. The steel panel was placed upside down, 14 cm from the nozzle of the burner. A piece of insulation was put on the top of the plate. In the middle of the insulation, a rectangular opening (23 mm × 67 mm) was cut to measure the temperature on the back side of the steel plate with an IR sensor (testo, Quicktemp 826-T2). The IR sensor measured the temperature in a range from room temperature up to ~ 220°C. The temperature was recorded for every 15 s.

The foam heights were determined using a ruler. The maximum foam height corresponds to the area where the foam had raised the most and the minimum foam height corresponds to the area where the foam had raised the least.

Rheology

A Stress Tech 299 Rheometer was used. The sample of paint was dried and grounded into fine pieces. About 0.5 g was pressed under 10 bars into a 1-mm thick tablet with a diameter of 15 mm. The tablet was placed between the parallel plates of the rheometer at 220°C. The rheometer was stress-controlled with amplitude of 100 Pa. The temperature ramp was set to increase from 220 to 350°C at a rate of 10°/min. The frequency was set to 1 Hz.

RESULTS AND DISCUSSION

Temperature development

In the comparison of temperature development between the three different carbon donors, penta,

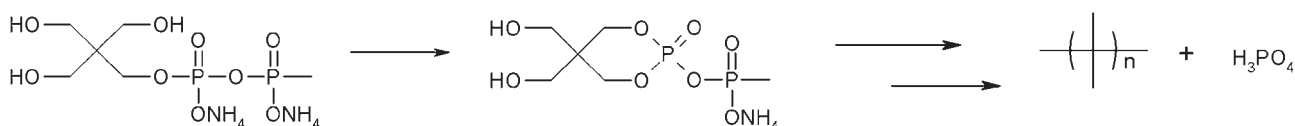


Figure 2 Ring closing esterification of the phosphorus ester and subsequent reduction to a carbon network.

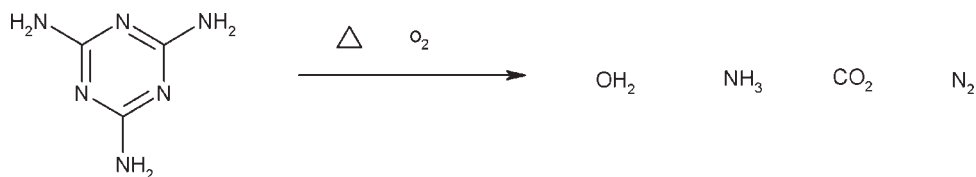


Figure 3 Degradation of melamine.

di-penta, and tri-penta, it is clear that the formulation containing penta can be kept at a lower temperature for a longer time when compared with the other formulations (Fig. 5). The di-penta formulation has a more rapid temperature increase and tri-penta has the most rapid temperature increase.

There is a distinct difference in foam height, which can be connected to the temperature differences, between the penta formulation and the two other formulations (di-penta and tri-penta) as can be seen in Figure 6. But the foam height variation between the di-penta and tri-penta foams is not noticeable, indicating that the temperature variations in the graph cannot exclusively be explained by foam height. Other factors than the foam height determine the insulating ability and temperature development in this case. The morphology and cell structure of the foam can most likely explain the differences in temperature development between the di-penta and tri-penta formulations.

The differences in swelling between the samples can be explained by the degree of functionalization of the penta compounds. It is believed that a high ratio of OH groups on the carbon source leads to a good intumescence. Pentaerythritol is the compound most

rich in hydroxyl groups, which coincides with the most efficient intumescence. However, this effect was taken into account when preparing the formulations, so that the same amounts of OH groups were added to each formulation, resulting in a larger weight amount of di-penta and tri-penta added to the formulations, respectively, compared to penta. However, the dry weight ratios between the remaining components were kept constant. Only the water contents had to be varied to obtain satisfactory coatings. The reason for the di-penta formulation still not swelling to the same degree as the penta formulation can be explained by the larger physical size of di-penta. If the reaction between di-penta and APP takes place previous to the degradation of di-penta into two penta molecules, there can be lack of space for the di-penta molecules to react with every sequence of the APP, resulting in an unreacted di-penta.

Another possible explanation for the more efficient intumescence of the penta formulation is the fact that the intumescent process is diffusion-controlled, leading to a slower and more inefficient intumescence of the bigger di-penta containing coatings. The poor foaming ratios of di-penta and tri-penta formulations can be explained by the excess of carbon donor

TABLE I
Intumescent-Coatings Formulations

Component	Penta (wt %)	Di-penta (wt %)	Tri-penta (wt %)
Exolit AP 422 ^a	23	22	16
Charmor PM15 ^b	8		
Charmor DP15 ^c		10	
Tri-pentaerythritol			8
Melamine	7	7	5
Mowilith DM 230 ^d	22	21	22
Kronos 2190 ^e	6	6	4
Natrosol 250 HR ^f	4	4	1
Sodium hexametaphosphate	1	1	1
Aerosil 200 ^g	0.5	0.5	0.4
Butylglycol	1	1	1
Water	28	27	40
Dry content	57	58	47

^a Ammonium polyphosphate.

^b Pentaerythritol.

^c Di-pentaerythritol.

^d Poly(vinylacetate).

^e Titanium dioxide.

^f Hydroxyethylcellulose.

^g Silica.



Figure 4 Overview of the Bunsen experiment setup.

because of the unreacted di-penta and tri-penta, which cannot be lifted up by volatiles as the network can.

Rheology

The results of the rheological characterizations are presented in Figures 7-9. The most striking result is

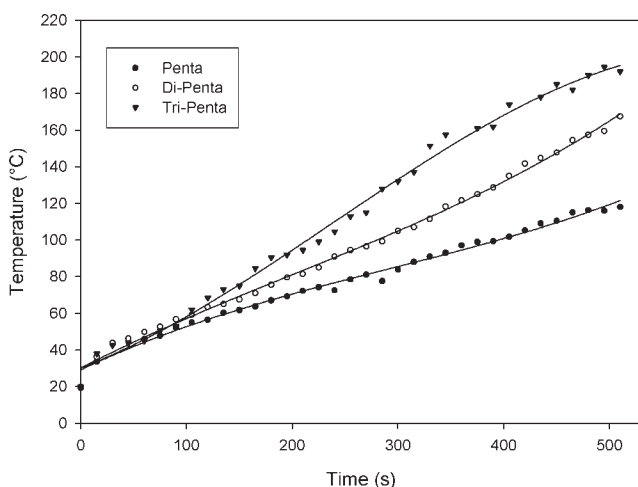


Figure 5 Temperature development comparison between formulations containing pentaerythritol/di-pentaerythritol/tri-pentaerythritol.

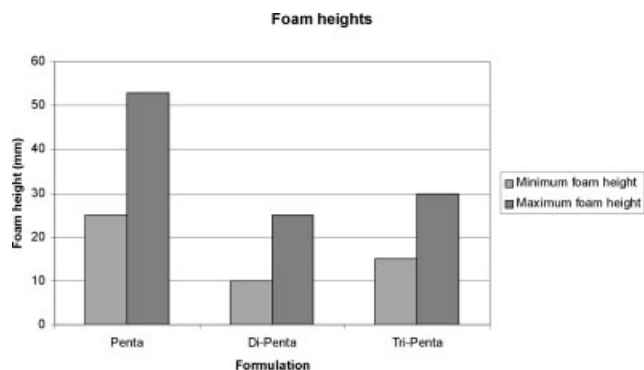


Figure 6 Foam heights of the formulations with varying carbon donor.

the shifting towards higher temperature for the phase maximum, the minimum dynamic modulus, $|G^*|$, and the crossover temperature between the storage modulus, G' , and the loss modulus, G'' , when replacing penta with di-penta and with tri-penta, respectively, in the formulations.

The temperature at the phase maximum represents the point at which the foaming material has reached its least elastic state (Fig. 7). This was supported by DSC analysis, showing a melting temperature of 266°C for penta. The rapid decrease in the phase angle represents the intumescent process, where the material becomes more and more elastic as a carbon polymeric network is formed. This corresponds to a major weight loss seen in the TGA measurements of the three formulations. At the point where G' and G'' cross, the foam has reached its most stable point, and from this temperature onwards, the foam degrades and loses its strength. At these crossover temperatures, a rapid weight loss

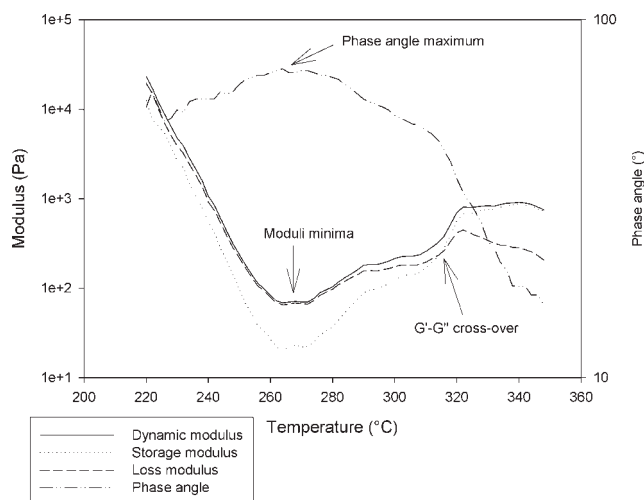


Figure 7 Overview of the rheology measurement of the pentaerythritol formulation.

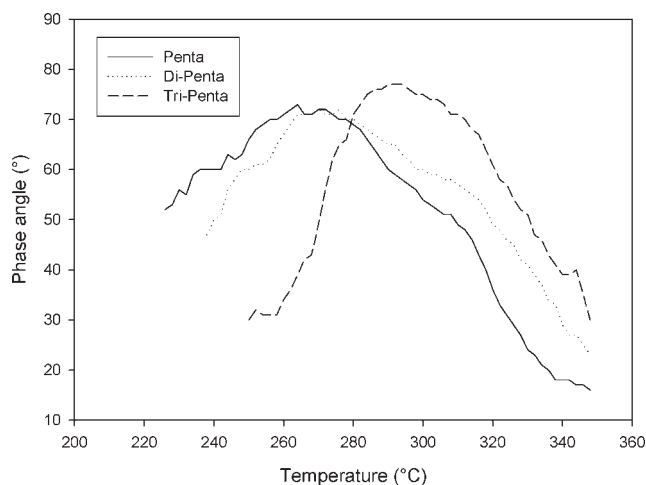


Figure 8 Phase angle measurements as a function of time for the formulations containing pentaerythritol, di-pentaerythritol, and tri-pentaerythritol.

step can be observed in the TGA measurements of the three formulations.

Cracking of the swollen foams is a problem, particularly on certain shapes of steel girders where the surface area of the foam needs to be larger than the surface area of the substrate, such as cylindrical beams.¹⁰ Delaying of cracking until a latter phase of the fire is beneficial since it saves time to fight the fire. Once the foam cracks, the temperature of the steel elevates rapidly at the cracking point, causing the mechanical strength of the steel to deteriorate fast. Tri-penta could possibly have an application in formulation used on pipes, etc., since the crossover temperature is shifted to a higher temperature when compared with the penta formulation.

Evident from the graphs (Fig. 7) is that the penta formulation has the longest intumescent time, followed by the di-penta formulation and then the tri-penta formulation. The temperature range of intumescence is calculated as the temperature at the crossover temperature minus the temperature at the maximum phase degree point (Table II). If the size differences between the different carbon sources are a crucial factor for efficient intumescence, this could explain why the penta formulation stays in the intumescent process longer than di-penta and tri-penta. If the space available around the APP is limited, penta will have

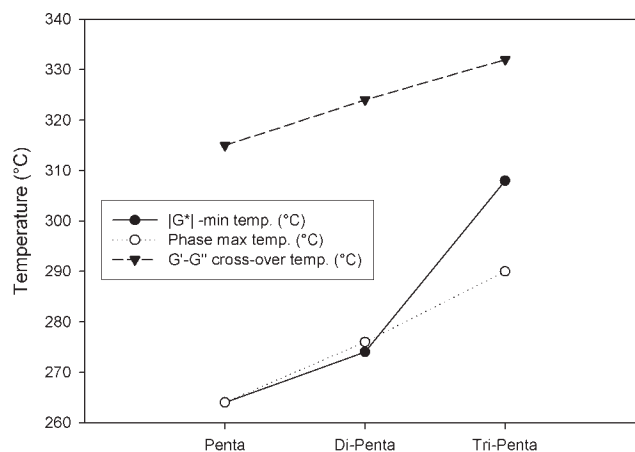


Figure 9 Rheological characteristics comparison among the three formulations.

the maximum number of molecules reacting, since it takes up the least space.

At the temperature where G' and G'' are equal or cross one another the complete three-dimensional network has been formed and from this point forward, the material will become increasingly elastic and less viscous.¹¹ The decrease in viscosity can be seen as a maximum of the dynamic viscosity coinciding with the crossover temperature. For intumescent foams, it would be desirable with a crossover temperature at a temperature as high as possible since the material is degrading from that point and on. A problem with intumescent foams is that they are porous and very fragile and can only withstand limited action of wind streams in a fire. Foam, which crossover temperature appears at a higher temperature, could possibly withstand the wind streams for a longer period than those with a crossover temperature at a lower temperature. This suggests that tri-penta, having a crossover temperature at a high temperature, could have applications in the use of intumescent coatings on cylindrical beams where the risk of crack formation is large.

CONCLUSIONS

The study of intumescent coatings has resulted in penta being the most desirable carbon source among the ones investigated. Penta has several positive

TABLE II
Rheological Characteristics of the Formulations Containing Penta, Di-Penta, and Tri-Penta

Formulation	$ G^* $ -min. temp (°C)	Phase max. temp. (°C)	$G'-G''$ crossover temp. (°C)	Temperature range of intumescence (°C)
Penta	264	264	315	51
Di-penta	274	276	324	48
Tri-penta	308	290	332	42

impacts on the coatings, e.g., a slow temperature development and a large foaming ratio.

The rheometer tests performed indicate that the penta formulation enters the intumescent process at a lower temperature and maintains in it during a broader temperature range than the di- and tri-penta formulations. The crossover temperature, the temperature at which the entire carbon network has been formed and starts to degrade, is shifted towards higher temperatures when replacing penta with di-penta and tri-penta, respectively, in the formulations.

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