PHOSPHORUS CONTAINING FLAME RETARDANTS IN EPOXY RESINS. EFFICIENCY AND INFLUENCE ON MATERIAL PARAMETERS

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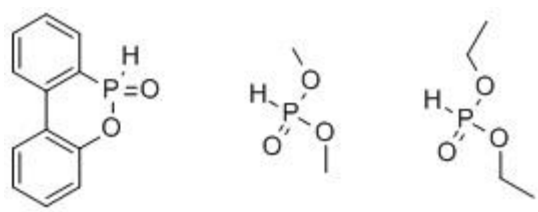
Abstract

Several star-shaped multifunctional phosphorus containing flame retardant additives were synthesized via Phospha-Michael addition, based on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), dimethyl phosphite (DMP) and tetra-[(acryloyloxy)ethyl] pentarythrit (PETA), or the heterocyclic tris-[(acrylocloxy)ethyl] isocyanurate (TAEI) as central building block. Phosphonates are of great interest, because they are able to increase the glass transition temperature of cured resins by crosslinking in a post curing step. RTM6®, which is commercially available and used by the Aviation Industries, was selected as a premixed epoxy system. The influence on the glass transition temperature was investigated.

1. Introduction

1.1. Phosphorus containing flame retardants

Due to their good flame retardant efficiency and minimal influence on the material properties of the matrix, e.g. glass transition temperature (T_g), bridged as well as oligomeric phosphorus containing compounds are widely used as flame retardant additives for epoxy resins.



DOPO DMP DEP

Figure 1. Flame retardant active phosphorus containing compounds.

Bridged phosphinates based on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, P.1, Fig. 1) account for a high gas phase activity and show excellent flame retardant performances, but tend to reduce the T_g of the cured epoxy resin, [1].

Phosphonates like dimethyl phosphite (DMP, P.1, Fig. 1) or diethyl phosphite (DEP, P.1, Fig. 1) are able to form polyphosphoric acids during pyrolysis and represent condensed phase active flame retardants. In contrast to DOPO, they exhibit a special post-curing behavior. They are able to improve the network density and increase the T_g by a transesterfication reaction with hydroxyl groups of the cured epoxy resin, [2]. Therefore, phosphonates function as reactive crosslinkers.

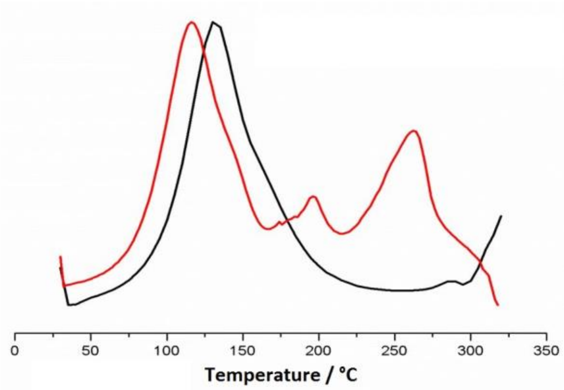


Figure 2. Curing process of a DGEBA/DMC-formulation without DEP (black) and with (red) DEP, [3].

The black curve, measured by Differential Scanning Calorimetry (DSC) in figure 2 belongs to a curing reaction of an epoxy system consisting of diglycidylether of bisphenol A (DGEBA) and 2,2'-dimethyl-4,4'-methylene-bis-(cyclohexylamine) (DMC), a system typically used by the Automotive Industry. An intense peak rises during the curing reaction. The red curve belongs to the same system, but additionally contains the phosphonate DEP (2 wt.-% of phosphorus). Now two additional peaks appear at higher temperatures. The peak at about 200 °C can be related to the crosslinking reaction, which is responsible for increasing the T_g. The peak at approximately 270 °C on the other hand is related to the decomposition of DEP, [3].

1.2. Multifunctional phosphorus containing flame retardants

Compared to more spherical monofunctional phosphorus compounds, so-called rod-like or star-shaped di- and multifunctional compounds have higher thermal stabilities, a lower plasticizer effect, and fewer tendency to migrate out of the material. Furthermore these introduced compounds are soluble in the epoxy resins and suitable for Resin Transfer Molding (RTM) processing. Depending on the chemical environment of the phosphorus atom the additives have a stronger gas phase or condensed phase effect of flame retardancy. The use of these different active substances is determined by the thermoset network and the reinforcement. In general, carbon fiber reinforced epoxy resins require more gas phase active flame retardants. Bridged phosphinates based on DOPO account for a high gas phase activity, but reduce the T_G. Polymeric derivates based on DOPO show less influence on the T_g, while maintaining the flame retardant efficiency, [4].

2. Experimental

2.1. Synthesis of multifunctional phosphorus containing flame retardants

Four star-shaped multifunctional phosphorus containing flame retardant additives were synthesized. Two of them containing DOPO and two others with the phosphonate DMP for an additional increase of the T_g. The schematic synthesis of the substances is shown in figure 3.

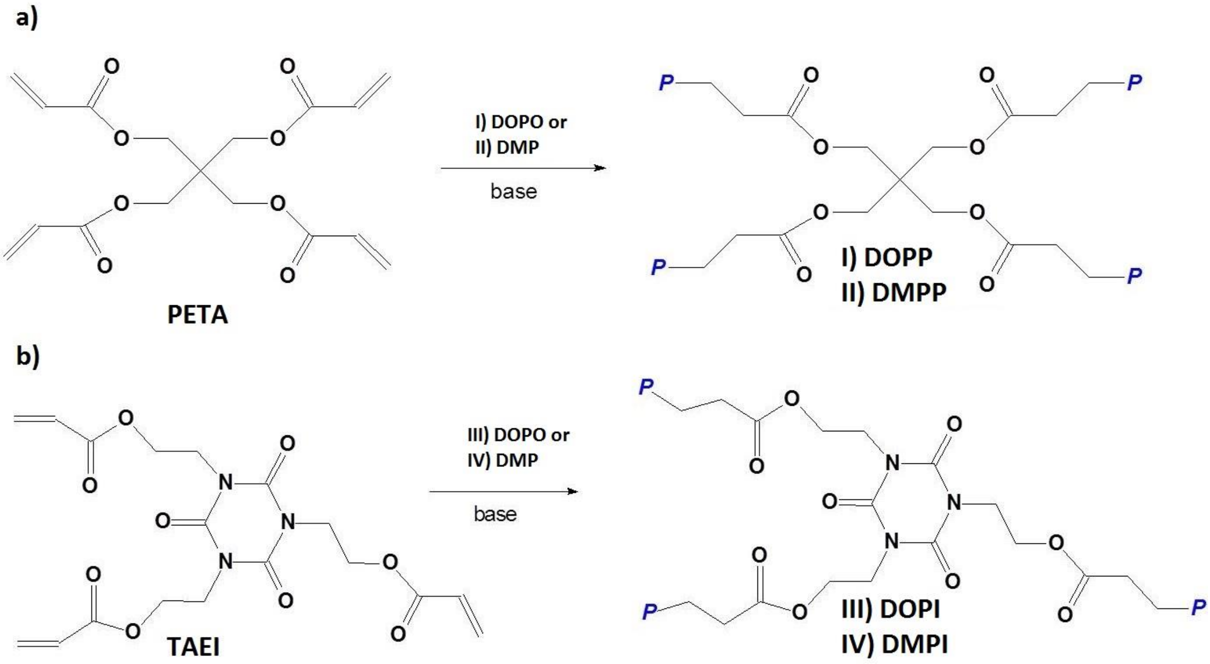


Figure 3. Reaction of a) *tetra*-[(acryloyloxy)ethyl] pentarythrit (PETA) with DOPO → **DOPP**, with DMP → **DMPP** and b) *tris*-[(acrylocloxy)ethyl] isocyanurate (TAEI) with DOPO → **DOPI**, with DMP → **DMPI**, [5,6].

In part a) *tetra*-[(acryloyloxy)ethyl] pentarythrit (PETA) and in part b) *tris*-[(acrylocloxy)ethyl] isocyanurate (TAEI) were used as central building block.

The Phospha-Michael addition reaction of DOPO with multifunctional acrylates like PETA and TAEI is well known and can easily be accomplished in the presence of triethylamine as base or without base and solvent via microwave synthesis, [4,5]. A synthesis with DMP could not be achieved using this method. An alternative route with 1,5,7-triazabicyclo[4.4.0]dec-5-en (TBD) as an auxiliary base was used to successfully obtain the products, [5,6].

The produced star-shaped multifunctional phosphorus containing flame retardant were characterized by NMR, matrix assisted laser desorption/ionization, time-of-flight mass spectrometry (MALDI-TOF MS) and elemental analysis, [4,6].

2.2. Preparation and curing of the resin and flame retardant mixture

All four prepared flame retardants were added and completely dissolved in RTM6® and degassed, till a homogeneous mixture was obtained. The final product contained 1 wt.-% of phosphorus. Then the resins were cured, whereby the mixtures containing DMP were additionally treated with a post-curing step at 200 °C for 1 h or at 215 °C for 100 min. The glass transition temperatures were measured via DSC and Dynamic Mechanical Analysis (DMA, T_g (3 Hz, 3 °C/min), [4,5,6].

2. Results and Discussion

As expected, the DOPO based additives exhibited a decrease in the glass transition temperatures of the cured epoxy resins. The black curve in figure 4 represents the cured RTM6®, the two other curves RTM6® blended with DOPP and DOPI.
In comparison, DOPP, raised from PETA and DOPO, causes a slightly lower T_g reduction than DOPI, raised from TAEI and DOPO, [6].

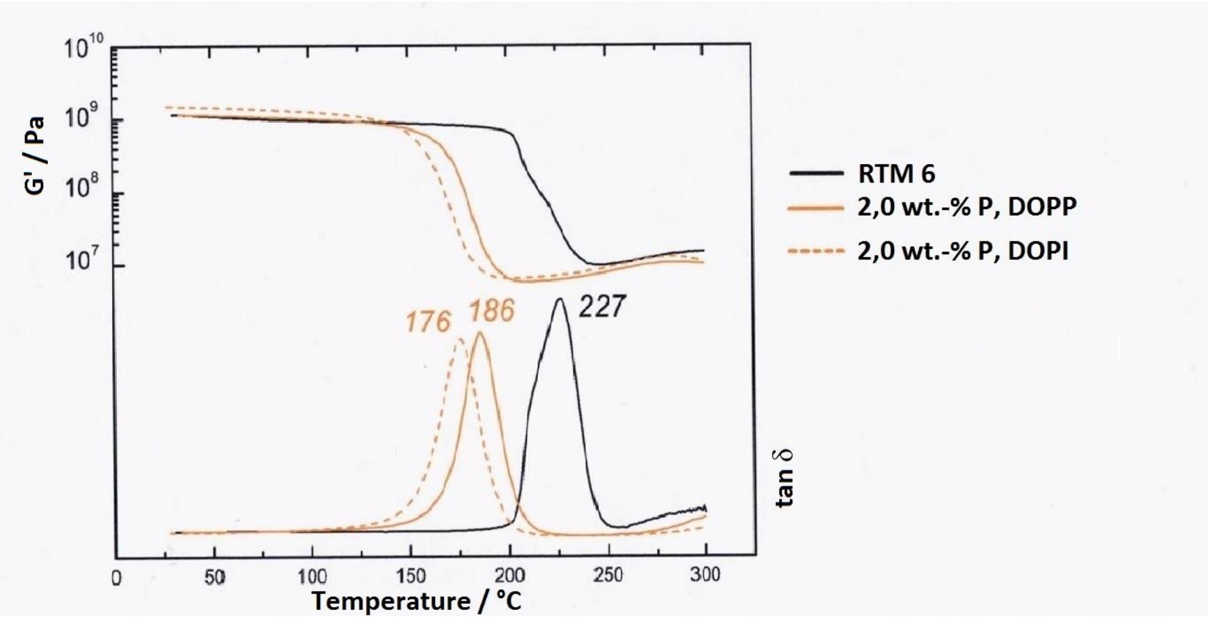


Figure 4. DMA-measurement of cured RTM6® and RTM6® blended with DOPP and DOPI, containing DOPO as building block.

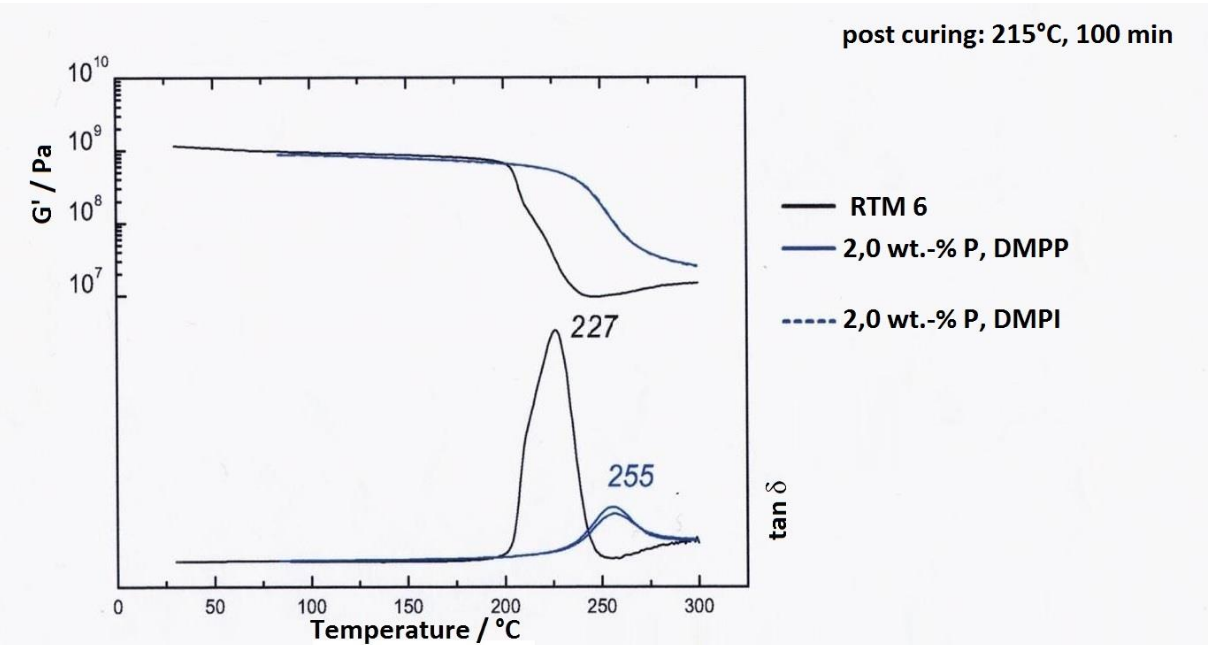


Figure 5. DMA-measurement of cured RTM6® and RTM6® blended with DMPP and DMPI, containing DMP as building block.

The reaction of PETA and TAEI with DMP instead of DOPO result in a total different behavior. As can be seen in figure 5, the T_g is increased by the transesterfication reaction of the DMP-groups with the polymer backbone, [6].

Testing of other acrylates are currently under investigation. Further results will be presented.

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