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Thermal degradation and fire behaviour of unsaturated polyesters filled with metallic oxides

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ABSTRACT

Nano-alumina and submicron alumina trihydrate particles were incorporated into an unsaturated polyester resin at various loadings. The morphologies of composites showed that only nano-alumina was correctly dispersed. The thermal degradation behaviour of the composites was studied using thermogravimetric analysis and Py-GC/MS, while their fire behaviour was investigated using cone calorimeter and pyrolysis combustion flow microcalorimeter. Synergistic effects on thermal stability and heat release rate were observed for combinations between both submicron filler and nanofiller. The best result for fire behaviour was obtained for a global loading of 10wt% with an equal mass ratio for both kind of particles. Mass loss curves also showed increased char yield. The interest of combining particles with different sizes has been discussed as well as the role of water release, regarding activations energies of degradation processes.

1. Introduction

Unsaturated polyester resins (UPR) are frequently used as polymer matrices in glass-fibre reinforced composites, in automotive or railway applications for example, because of their excellent processability and low cost. Due to their common use, they are often brought into fire situation. High levels of flame retardancy are currently achieved with halogenated compounds, such as chlorendic acid or tetrabromophthalic anhydride, combined with antimony trioxide [1]. Nevertheless, due to environmental and toxicological concerns, as well as risks of emission of corrosive products, the future of these compounds is compromised. Micron-sized fillers such as alumina trihydrate are also effective, but only at high loadings, leading to too high viscosities for good processing conditions, too high density, and loss of mechanical properties in the absence of any surface modification [2]. Thus, the development of new solutions for improving flame retardancy is needed and the use of nanofillers and also submicron fillers seems a promising alternative.

Many investigations about the interest of nanoparticles to improve fire retardancy have been performed on thermoplastic polymers, but only few works concern the fire behaviour of unsaturated polyesters filled with nanoparticles.

Commercial organomodified montmorillonites (oMMT) have been used in a wide range of polymers, and also tested in unsaturated polyesters [3]. The influence of the oMMT concentration on physical properties, and thermal stability in particular was studied. TGA analyses showed that onset degradation temperatures (T_{onset}) can be increased by increasing oMMT concentration up to values causing aggregation. This has been ascribed to the barrier effect of MMT on mass transfer of degradation products to delay the thermal decomposition of UPR as well as their char promoting action. Combining oMMT with flame retardants such as ammonium polyphosphate and smoke suppressants can lead to a synergistic effect and a noteworthy improved thermal behaviour [4]. Carbon nanofibres were also used to reduce the flammability of UPR [5].

Recently, layered double hydroxides (LDH) also proved their efficiency to improve fire retardancy of unsaturated polyesters [6]. Two organomodified LDH were introduced into a UPR resin at two concentrations. Increase in thermal stability was observed, but was not linked to the amount of fillers. With only 1wt% LDH, pHRR was reduced up to 47%.

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Table 1
Characteristics of the fillers.

	Specific surface area (m^2/g)	Median particle size (nm)
ALuC (AL)	100	13
ATH (AT)	22	300
Silica (SI)	150	12

Table 2
UPR compositions (wt %).

Sample	Resin	AL	AT	deAT	SI
Unmodified resin	100				
5AL	95	5			
5AT	95		5		
2,5AL2,5AT	95	2.5	2.5		
10AL	90	10			
10AT	90		10		
5AL5AT	90	5	5		
10AL10AT	80	10	10		
5AL5deAT	90	5		5	
5SI5AT	90		5		5

If it can be expected that some of the mechanisms established for thermoplastic polymers are transferable to thermosets, e.g. barrier effects that would only result from polymer ablation during combustion, while other effect such as changes in the polymer viscosity and migration processes of nanoparticles towards material surface seems excluded. In addition, some phenomena must be exclusively considered in thermosets such as interactions between nanoparticles and the cross-linked network.

The present work concerns nanometric metallic oxides (mainly aluminium oxides) which are another kind of commercial nanoparticles. These fillers have been deeply used in various polymers such as PMMA [7,8], PS [8], vinyl ester resins [9]. Heterogeneous catalysis mechanisms due to hydrogen bonding between the polymer and the hydroxyl groups at the particles surface were considered in order to establish their mode of action. The presence of oxides seems to modify the degradation pathway of PMMA by decreasing the quantity of evolved methyl methacrylate and increasing the production of methacrylic acid and methanol.

To investigate the influence of aluminium oxide nanoparticles in UPR and the possibility of synergistic effects on thermal degradation behaviour and fire properties with submicron aluminium hydroxide particles, each kind of particles was incorporated alone or in combination with the other one, and the above properties have been evaluated and discussed.

2. Experimental

2.1. Materials

Orthophthalic based unsaturated polyester (commercial name Aropol G174-2), with a styrene content of 38wt% was kindly supplied by Ashland Polyester. Alumina (Aerosil AluC noted AL) from Evonik, Alumina trihydrate (Apyral 200SM, noted AT) from Nabaltec, and a fumed silica treated with a methacrylsilane (Aerosil R711 noted SI) from Evonik were dried one night at 100 °C before use. Specific surface area and median size of particles are given in Table 1. Dehydrated ATH (deAT) was obtained heating ATH one night at 600 °C.

2.2. Sample preparation

Unsaturated polyester was blended by mechanical stirring (800 rpm) for an hour at room temperature with the desired amount of additives, which were slowly added. To improve dispersion and remove bubbles, the samples were placed in an ultrasonic bath for 5 min.

After adding the required amount of catalyst and initiator, the samples were cast in glass moulds and cured at room temperature then post cured at 60 °C for 8 h and at 100 °C for 2 h.

The different compositions of the composites are gathered in Table 2.

2.3. Methods

Micrographs of nanocomposites were obtained with a SEM microscope (FEI Quanta 200 SEM) equipped with a scanning transmission electron microscopy detector (STEM). All images were obtained under high vacuum at a voltage of 25.0 kV with a spot size of 2.8 nm and a working distance of 7.6 mm.

Thermogravimetric analysis was performed using a Perkin Elmer Pyris-1 TGA thermobalance for samples of 10 ± 2 mg. For each sample, two runs were carried out at a heating rate of 10 °C/min from room temperature to 800 °C under a gas flow (nitrogen or air) of 20 mL/min.

A Pyroprobe 5000 pyrolyser (CDS Analytical) was used to flash pyrolyse the samples in a helium environment. This pyrolyser is supplied with an electrically heated platinum filament. One coil probe enables the pyrolysis of samples (less than one mg) placed in a quartz tube between two pieces of rockwool. The same sample was successively heated at 250, 380, 430, 580 and 900 °C. These temperatures were chosen according to the TGA curves. Each temperature was held for 5 s then the gases were drawn to the gas chromatograph for 5 min. The pyroprobe 5000 is interfaced to

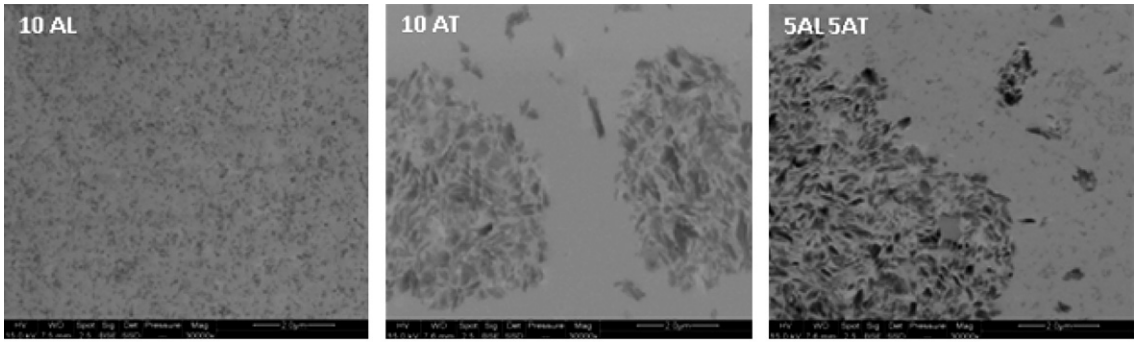

Fig. 1. STEM micrographs of the UPR formulations.