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Novel composites from green unsaturated polyesters and fly ashes: Preparation and characterization

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ABSTRACT

New composites from unsaturated polyesters (UPs), with high 'green' content, and fly ashes (FA) were studied for the first time. All the monomers used in the synthesis (fumaric acid, succinic acid, propylene glycol, 1,3-propanediol) can be obtained from renewable resources, with the exception of diethylene glycol. The composites were prepared by crosslinking the UPs in the presence of FA, using styrene (St), methyl methacrylate (MMA) and a mixture of acrylated epoxidized soybean oil (AESO) with St as reactive solvents. The results showed that the incorporation of the FA improved the thermal stability of the composites. Regarding the thermomechanical properties, it was found that the incorporation of 50% (w/w) FA led to composites with higher elastic modulus (E′) and higher glass transition temperature (T_g) than the neat polymeric matrix. These observations indicate a good compatibility between the FA and the polymeric matrix.

1. Introduction

Unsaturated polyester composites (UPCs) are widely used materials in various areas/industries (*e.g.* building and automotive industries, naval constructions). The interest in UPCs is mainly due to their simple and straightforward production, at very affordable costs. The properties of the UPCs can be easily tuned by using unsaturated polyesters (UPs) with different compositions, diverse crosslinking agents and/or fillers. Currently, the monomers employed to prepare UPs that are further used in the UPCs preparation have a petrochemical origin, which can be seen as a serious disadvantage not only from an economic standpoint, due to the constant oil price fluctuations, but also from an environmental perspective. To overcome or mitigate such disadvantages, in the last years, several UPs based on 'green' monomers, *i.e.* derived from biomass, have been synthesized [1–4]. Different fillers have been used in the preparation of UPC, namely glass fiber [5], montmorillonite [6], natural fibers (*e.g.*, kenaf fiber [7]), and fly ashes (FA) [8–12]. Particularly, the use of FA as a filler in UPCs has significant advantages from both an environmental and economic standpoints. Considering the environmental aspect, their use in UPC allows the 'appropriate disposal' of a residue that is produced in large quantities during the coal burning. Additionally, FA is an inexpensive raw material [8,13,14], turning the new composites extremely cost effective. In literature are reported some works dealing with the preparation of UPCs with FA. Guhanathan and Devi [8] prepared UPCs making use of FA treated with different silanes, and the results have shown that such UPCs have similar properties to those presented by UPCs reinforced with the conventional calcium carbonate filler. In another work, Ramakrishna et al. [9] compared the performance of FA reinforced UPCs with those reinforced with granite powder, and they have found that the former group of UPCs had better flexural and tensile strengths than the latter ones. More recently, Ray [10] has shown that the addition of styrene-butadiene rubber latex to UPCs reinforced with FA contributed to an increase in the damping properties of the UPCs, as evidenced by the dynamic mechanical thermal analysis (DMTA). In the same line of research, Ghorui et al. [12] used maleated castor oil in UPCs reinforced with FA in order to augment the damping properties of the composites. In this work, the main aim was the preparation of UPCs based on 'home-made' UPs, with 'high green' content, and FA. To the best of our knowledge, the use of 'green' UPs in the preparation of UPCs has never been reported. Additionally, it is proposed the use of a mixture of acrylated epoxidized soybean oil (AESO) and different monomers (styrene (St) and methyl methacrylate (MMA)) as reactive solvent (RS), which constitutes an important novelty of the work. The structure of the UPs was characterized by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopies. The thermal properties of the UPs and UPCs were evaluated by thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA), to allow a detailed characterization of the viscoelastic properties of the UPCs. The study of such properties will contribute for the development of the field of high performance UPCs reinforced with FA.

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Table 1
Main characteristics of the FA.

Compound	Weight percent
SiO_2	48
Al_2O_3	18.9
Fe_2O_3	8.8
CaO	9.7
MgO	2.1
K_2O	1.9
Na_2O	1.1
TiO_2	0.93
MnO	<0.3
P_2O_5	0.4
Organic matter (loss on ignition)	5.6

2. Experimental

2.1. Materials

Fumaric acid (FuA, 99%), succinic acid (SA, 94.5%), diethylene glycol (DEG, 99%), propylene glycol (PG, 99%), acrylated epoxidized soybean oil (AESO), and potassium hydroxide (KOH, 85%) were purchased from Sigma-Aldrich (St Louis, USA). 1,3-Propanediol (PDO, 98%) was purchased from TCI Europe (Zwijndrecht, Belgium). Styrene (St) and methyl methacrylate (MMA) were purchased from Acros Organics (Geel, Belgium). Ethanol (EtOH, 96%) was purchased from Panreac (Barcelona, Spain). Benzoyl peroxide (BPO, 97%) was purchased from Fluka (St Louis, USA). Phenolphtalein was purchased from Riedel-de-Häen (Seelze, Germany). Deuterated THF (THF-d_8) was purchased from Eurisotop (Saint Aubin, France). Hydroquinone was purchased from Analar. All the reactants were used as received, unless otherwise stated. The fly ashes, type F, were obtained from Pego steam power plant (Pego, Portugal) and their main characteristics are presented in Table 1.

2.2. Synthesis of the UPs

The UPs were prepared by bulk polycondensation, performed in a 250 mL four head reactor and equipped with an anchor blade mechanical stirrer, a nitrogen inlet, and a condenser attached to a round-bottom flask to collect the water. The reactor was heated using a silicon oil bath. The diacids, diols and the inhibitor were placed in the reactor and were heated up to a maximum temperature of 210 °C, for different reaction times. The end of reaction was set when the acid value (AV), determined according to the standard ASTM 109-01, reached a constant value. Table 2 presents the molar amounts of monomers, temperatures and reaction times used in the polycondensation reactions.

2.3. Preparation of the composites

The UP was dissolved in the reactive solvent (RS). Then, the initiator (BPO) was added in a weight percentage of 3% w/w (relative to the mass of UP + RS). Once the BPO was dissolved, a measured amount of FA was uniformly dispersed in UP/RS mixture, by stirring. The mixture was placed into a teflon mold with dimensions (16 × 7 × 0.5) mm and was put in an oven at 80 °C, for 2 h and 3 h for the formulations containing UP1 and UP2, respectively. After cure, the UPCs were removed from the mold and the edges were trimmed. The same method was used when AESO was added as co-RS. The compositions of the composites are given in Table 3.

Table 3
Composition of the different unsaturated polyester resins (UPRs) and UPCs.

Composite	UP	RS	Co-RS (AESO)	w_{UP}/w_{RS}	w_{RS}/w_{AESO}	FA (% w/w)
UPR 1	UP1	St	–	50/50	–	0
UPC 1						15
UPC 2						25
UPC 3						50
UPR 2		MMA	–	50/50	–	0
UPC 4						15
UPC 5						25
UPC 6						50
UPR 3	UP2	St	–	50/50	–	0
UPC 7						15
UPC 8						25
UPC 9						50
UPR 4		MMA	–	50/50	–	0
UPC 10						15
UPC 11						25
UPC 12						50
UPR 5	UP1	St	–	63/37	–	0
UPC 13						15
UPC 14						25
UPC 15						50
UPR 6		MMA	–	63/37	–	0
UPC 16						15
UPC 17						25
UPC 18						50
UPR 7	UP2	St	–	63/37	–	0
UPC 19						15
UPC 20						25
UPC 21						50
UPR 8		MMA	–	63/37	–	0
UPC 22						15
UPC 23						25
UPC 24						50
UPR AESO 20	UP1	St	AESO	50/50	80/20	0
UPC AESO 20						15
UPR AESO25					75/25	0
UPC AESO 25						15
UPR AESO 30					70/30	0
UPC AESO 30						15
UPR AESO 35					65/35	0
UPR AESO 35						15

2.4. Characterization techniques

The chemical structure of the UPs was analyzed by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopies. FTIR spectra were obtained in the range 4000–500 cm^{-1} at room temperature using a Jasco FT/IR-4200 spectrometer, equipped with a Golden Gate Single Reflection Diamond ATR. Data collection was performed with 4 cm^{-1} spectral resolution and 64 accumulations.

^{1}H NMR spectra of the UPs were obtained at 25 °C on a Bruker Avance III 400 MHz spectrometer using a 5 mm TIX triple resonance detection probe, in THF-d_8. Tetramethylsilane (TMS) was used as internal standard.

The thermal stability of the UPs and UPCs was evaluated by TGA, using a TA Instruments Q500 thermogravimetric analyser (thermobalance sensitivity: 0.1 μg), which was previously calibrated in the range 25 °C to 1000 °C by running tin and lead as melting

Table 2
Reaction conditions for UP1 and UP2.

Formulation	n_{PG} (mol)	n_{diol2} (mol)	n_{SA} (mol)	n_{FuA} (mol)	$n_{hydroquinone}$ (mmol)	t (h)	T (°C)	AV (mgKOH/g)
UP 1	0.25	0.29 (DEG)	0.24	0.22	0,3	5.00	200	35.72
						2.50	210	
UP 2	0.25	0.29 (PDO)	0.24	0.22		5.00	200	30.79
						2.00	210	