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Improving the flame retardancy of flax fabrics by radiation grafting of phosphorus compounds

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ABSTRACT

Two phosphorus-based molecules were grafted onto flax fibers through electron beam irradiation in order to impart flame retardancy to flax fabrics. Fabrics were impregnated by dipping them into a solution containing a phosphonated monomer: dimethyl(methacryloxy)methyl phosphonate (MAPC1) or dimethylvinyl phosphonate (MVP). Then fabrics were irradiated at a dose ranging between 10 and 100 kGy. The grafting efficiency was found to be dependent on the molecule concentration in the impregnation solution, on the radiation dose and on the nature of the monomer. In particular, it has been observed that MAPC1 is grafted only onto the surface while MVP is also grafted into the bulk leading to high phosphorus content (4 wt%). Flame retardancy of the modified flax fibers, fabrics and polyester thermoset composites containing these fabrics were also investigated. High phosphorus content allows fabrics to achieve self-extinguishing behavior. The flammability of composites in cone calorimeter test is also reduced, even if the thermoset is not flame retarded itself.

1. Introduction

After many years of high-tech development of artificial fibers such as carbon, aramid or glass, today's market trends are moving to the natural fibers [1]. The use of natural reinforcements in composite materials has considerably increased due to their numerous advantages [2–4]: renewability, biodegradability, low cost, low density, low abrasiveness (compared to fiberglass) and good mechanical properties. However, some disadvantages limit their industrial applications such as low compatibility with hydrophobic polymer matrix, the thermal sensitivity at the temperature of compounding process and the flammability [4,5].

Fiber surface modification could be a good alternative to solve several drawbacks of natural fibers like fiber–matrix compatibility and the flammability. The fiber surface modification can be performed by various treatments [1,6–8]: impregnation, chemical coupling (including silane [9,10]) corona [11,12], plasma [13,14], UV irradiation [15], gamma or electron beam irradiation [16–18].

Flammability of naturel fibers and biocomposites has already been reviewed [5,19,20]. Among different strategies to impart flame retardancy to natural fibers, phosphorus-based compounds have been pointed out. Suardana et al. have treated jute and coconut fibers with diammonium phosphate (DAP) [21]. The flame retardancy of polypropylene (PP) and poly(lactic

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acid) (PLA) composites containing these modified fibers was improved with the increasing DAP content. Matko et al. have also modified lignocellulosic fillers with DAP and incorporated them into polyurethane [10]. Limiting Oxygen Index (LOI) was significantly higher with the phosphorylation of fillers. A slight improvement of the flame retardancy of a PLA/thermoplastic starch blend containing flax fibers was achieved when fibers were previously treated with a phosphorus silane [9]. Dorez et al. have improved the flame retardancy of biocomposites by modifying flax fibers with various phosphorus-based compounds [22,23]. Moreover they proved that phosphonic acid can be efficiently grafted by reacting with hydroxyl groups of flax fibers surface [24]. Shimao et al. have flame retarded PLA composites containing ramie fiber with ammonium polyphosphate (APP) [25]. When APP is located only in the sizing of fiber, LOI increases from 19.1 to 25 but the composite is still unclassified according to UL-94 test. Rating V0 is obtained when APP is added into the matrix. Finally, when APP is present both in the matrix and in the fiber sizing, LOI reaches 35.6 and the composite is rated V0. Then the best performances are obtained when the fiber is flame retarded in addition to the matrix.

Several authors have also used the ionizing radiation to graft compounds (including flame retardants) onto fibers. A first method to graft molecules onto lignocellulosic fibers is called pre-irradiation. Khan has studied the grafting efficiency of methyl methacrylate (MMA) in pre-irradiated jute fibers [16]. Fibers must be maintained at low temperature (−20 °C) to preserve the radicals and peroxides after irradiation. The fibers are then immersed in the solution containing MMA. The grafting content reaches 70 wt% at 100 kGy in air when MMA concentration is fixed to 10 wt%. Nevertheless, to obtain such value, temperature must be as high as 70 °C. On the contrary, the grafting weight is close to 0% at 40 °C.

A second method consists in irradiating and grafting simultaneously. Fibers are firstly immersed in a solution containing the molecule to be grafted. After solvent evaporation, fibers are irradiated and grafting occurs during this treatment. Subsequent washing allows removing all non-grafted molecules. In the seventies, Liepins et al. have attempted to graft various bromine or phosphorus-based flame retardants onto poly(ethylene terephthalate) (PET) fibers by gamma irradiation [26,27]. According to the used procedure, they were able to graft only onto the surface, uniformly into the fiber or even only in the core. The location of the flame retardant and its nature were the two most important parameters influencing the flame retardancy (assessed only from limiting oxygen index measurements). Harris et al. have also grafted copolymer of vinyl phosphonate oligomer and N-methylolacrylamide (NMA) onto cotton fabric using an irradiation method. NMA promotes the grafting of the phosphonate monomer [17]. Phosphorus was located within fibrous cross section and the polymer add-on reached 46 wt% for a total monomer conversion at only 23 kGy. Mey-Maron et al. have grafted bromostyrene to polyester fabric using both pre-irradiation and simultaneous irradiation [28]. The amount of polybromostyrene grafted onto fabric reaches 19.3 wt% when fibers were pre-irradiated at 89 kGy. Simultaneous irradiation was much more efficient with 30.9 wt% of grafted polybromostyrene at only 35 kGy. The radiation grafting of vinyl phosphonate oligomer was also used by Kaji et al. to impart flame retardancy to a polyethylene open-cell foam [29]. Conversion of monomer was close to 97% and the degree of grafting was around 55%. Phosphonate was coating on the inner surface of the foam cell.

According to some works previously reported, vinyl phosphonates appear as good candidates to be radiation grafted onto fibers in order to improve their flame retardancy. In this study, we will manage the radiation grafting of two vinyl phosphonates (namely MAPC1 and MVP) onto flax fabrics and we will characterize the flammability of these modified fabrics. Finally the flame retardancy of thermoset composites containing these fabrics will be also assessed.

2. Experimental

2.1. Materials

Flax fabrics were kindly provided by Hexcel. The weight of fabrics was 200 g/m^2. The composition of flax fibers is 81 wt% of cellulose, 13 wt% of hemicellulose and 2.7 wt% of lignin in good agreement with the literature [30–33].

Dimethyl(methacryloxy)methyl phosphonate (MAPC1) (Specific Polymer), dimethylvinyl phosphonate (MVP) (see Fig. 1), tetrahydrofurane (Fisher Scientific) and ethanol (Fisher Scientific) were used as received without any purification.

The resin used in this study was a DCPD (dicyclopentadiene) isophtalic unsaturated polyester, Enydyne N50, supplied by Cray Valley. The matrix was polymerized with 1.8% w/w of methyl ethyl ketone peroxide (MEKP – Luperox K1S).

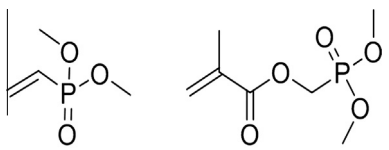

Fig. 1. Phosphorus-based molecules used in this study.