INVESTIGATION OF FLAME RETARDANCY OF POLYPROPYLENE-WOOD FIBRE COMPOSITES

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Abstract The flame retardancy of polypropylene-wood-fibre composites (CM) have been investigated. CM - new generation of materials - were prepared on a two-roll machine. Ammonium polyphosphate (APP I & II), melamine phosphate (MP), melamine diphosphate (MDP) and pentaerythritol (PER) were used as flame retardants. The experimental results show that the LOI values of the CMs increase in line MPP – MDP – APP I - APP II and the char former/blowing agent ratio has a great effect on the flame retardancy of the propylene-wood fibre composites.

INTRODUCTION

Wood-plastics composites are known as a new generation of materials for housewares, automotive and construction, etc. [1]. They combines the favourable performance and low cost attributes of both wood and plastics. In recent years, they have been developed rapidly, especially in North America. The interface compatibility between wood-fibre and polymers in wood-plastics composites is a key problem, on which a lot of literature and patents focus [2–5]. Maleic anhydride grafted polymers, such as maleated polyethylene and maleated polypropylene, are widely used as good compatilizers to improve the mechanical properties. Silicones, fatty acids and elastomers can also be used as compatibizers in wood-plastic composites. However, flame retardancy of wood-plastics composites is another important topic because of easy flammability of both woodflour (fibre) and plastics and demands of fire protection in their use.

Ammonium polyphosphate (APP), melamine diphosphate (MDP) and other phosphorus-nitrogen flame retardants are very effective flame retardants for wood, polyolefins etc. We report research on flame retardancy properties of polypropylene-wood-fibre composite treated with some phosphorus-nitrogen flame retardants.

EXPERIMENTAL

Materials

The following materials were used as received: melamine, ammonium dihydrogen phosphate, pentaerythritol and urea (reactant degree, supplied by Kanto Chemical, Japan), composite material (CM) containing 45 % of polypropylene resin and 55 % of wood-fibre as granulate product (supplied by Anex, Japan). Ammonium polyphosphate (APP form I & II) was made by literature method [6], melamine polyphosphate (MPP) and melamine diphosphate (MDP) were made by ourselves.

Preparation of MDP and MPP

a) Melamine diphosphate (MDP)

Heating of ammonium dihydrogen phosphate and melamine (molar ratio of ammonium dihydrogen phosphate to melamine 1:1) in electric furnace at 200 ° C for 4 hours was synthesized the melamine diphosphate.

b) Melamine polyphosphate (MPP)

The melamine polyphosphate was prepared by heating of melamine, urea, and dihydrogen phosphate (molar ratio of melamine to urea to dihydrogen phosphate 1:1:1) in an electrical furnace at 200° C for 4 hours. After cooling to room temperature in the desiccator, the crushed product was heated for 1 hour more at 300 ° C.

Sample Preparation

All samples were prepared by mixing composite material CM (45 % of polypropylene and 55 % of wood-fibre) and other additives on a two-roll mill (Test Mixing Roll Machine, type 191-TM) at a temperature range of 185–195 ° C for 15 min.

Sheets of about 135 x 85 x 3 mm were obtained by compression moulding on a curing machine for 45 min (the temperature decreased from 150 ° C to 100 °C) followed by cooling to room temperatures. Standard specimens were cut from the sheets for the limiting oxygen index measurements [7].

Limiting Oxygen Index

The limiting oxygen index (LOI) of all samples were tested on an oxygen index instrument (Oxygen index flammability tester, type No. 214) at room temperature.

The limiting oxygen index (LOI) was determined according to JIS K 7201-1,2 [7]. LOI is a parameter for evaluating flame retardancy and flammability of polymeric materials in the same conditions. It denotes the lowest volume concentration of oxygen sustaining candle-like burning of materials in mixing gases of nitrogen and oxygen.

X-Ray Diffraction

An X-ray powder diffraction pattern of powder samples were collected at room temperature with nickel filtered Cu K α radiation an Rigaku RAD—1B diffractometer.

Melamine and most of its derivatives such as melamine diphosphate, melamine polyphosphate etc. are highly crystalline materials. X-ray diffraction has been used to characterize APP I, APP II, MDP and MPP. The X-ray diffractograms of these compounds show Figures 1- 4:

Figure 1 XRD of APP I

Figure 2 XRD of APP II

Figure 3 XRD of MDP

Figure 4 XRD of MPP

Solid-State NMR Spectroscopy

Solid-state ^{31}P NMR spectra were recorded on a JEOL-EX400 FT-NMR spectrometer at 109.25 MHz at room temperature. The excitation pulse and recycle time were 4.6–4.8 μs (4–6 scans), respectively. ^{31}P shifts are referenced relative to 85 % $\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ at 0 ppm.

Whereas X-ray diffraction is mainly used for the investigation of crystalline materials, solid-state NMR is an effective tool for characterizing both amorphous and crystalline materials. Figures 5 and 6 show ^{31}P solid-state NMR spectra of melamine diphosphate (MDP) and melamine polyphosphate (MPP).

Figure 5 ^{31}P MAS NMR of MDP

Figure 6 ^{31}P MAS NMR of MPP

RESULTS AND DISCUSSION

Samples of composite material (CM) containing flame retardant (FR) [melamine phosphate, melamine diphosphate, ammonium polyphosphate I & II] and charring agent – pentaerythritol (PER) - were prepared by reacting CM with FR and PER at a two-roll mill at a temperature range of 185–195 °C for 15 min.

The structures of the reaction products are dependant on the reactants ratio. If FR/PER molar ratio is greater than or equals 2.0, the hydroxyl groups of PER can be consumed completely and a product without hydroxyl groups will be produced. But if MP/PER molar ratio is less than or equals 1.0, the hydroxyl groups of PER cannot be consumed completely and a product with hydroxyl groups. So, it can be control the char former/blowing agent ratio of flame retardant additives by changing the reactants ratio. In this way, the flame retardancy of compositions can be tailored.

Molar Ratio of FR and PER

As we know, when CMs are exposed to a fire, they will form a non-flammable, multi-cellular charred layer which provides an efficient shielding and insulation for the underlying polymer matrix against direct contact with fire and oxygen, as well as against the heat transfer. The multi-cellular charred layer is formed under the co-action of three components of CMs: the carbonization agent was dehydrated by the acid released from acid source and turned into char, and meanwhile the char was expanded by the inert gas generated from the blowing agent. Obviously, when FR/PER ratio decreases, the char former/blowing agent ratio of reaction products will be corresponding increased.

Flame Retardance

The limiting oxygen index (LOI), which is as a qualitative method to rank the flammability of materials, is the minimum oxygen concentration in an oxygen/nitrogen mixture that will just support the combustion.

Table 1 presents the LOI values of the flame retarded polypropylene-wood-fibre composites. It can be seen that the LOI values of the composites increase in line MPP – MDP – APP I - APP II. The LOI value of the composite containing 23.5 % APP II (P/N =1.5) and 5.9 % PET is as high as 36 %. Results illustrate that APP II has a very good flame retardancy.

TABLE 1 The limiting oxygen index (LOI) of composite material (CM) containing flame retardants (FR) and charring agent (pentaerythritol – PER)

BLEND (MASS RATIO) \ FR	APP I (P/N = 1.2)	APP II (P/N = 1.5)	APP II	MDP	MPP
CM : FR = 7 : 3	25.9	26.3	25	22.4	22.4
CM : FR : PER = 7 : 3 : 1	52.6	61.8	43	36.8	29.8
CM : FR: PER = 12 : 4 : 1	34.2	36.8	31.6	27.2	23.7
CM : FR: PER = 27 : 3 : 1	22.4	21.1	22.8	21.1	20.6

CM – composite material (45 % of polypropylene, 55 % of wood fibre)

FR – flame retardant (APP I – ammonium polyphosphate, form I; APP II – ammonium polyphosphate form II; MDP – melamine diphosphate; MPP – melamine polyphosphate)

PER – pentaerythritol

The LOI value increases from 20.6 % for CM:MP:PER = 7:3:1 to 36.8 % for CM:APP II (P/N = 1.5): PER = 12:4:1. The increase of LOI with a moderate amount of PER addition may be explained by the increase of the degree of expansion resulting in the formation of thicker insulating char, which separates the flame from the inner material more efficiently, and thus makes the flame retardance effectively improved. However, the char could be worsened by the excessive nitrogen volatiles formed during the combustion. It can be concluded that the increase in the concentration of nitrogen volatiles does not always imply better flame retardance. In other words a distinct synergistic effect exists between nitrogen and phosphorus.

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