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NATURAL FIBER REINFORCED TECHNICAL (BIO-)COMPOSITES MODIFIED WITH HALOGEN-FREE FLAME RETARDANTS

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Abstract

Under the aspect of sustainability and the use of alternative materials, engineering thermoplastics such as polybutylene terephthalate (PBT) will be reinforced with renewable raw materials such as regenerated cellulose fibers.

The University of Kassel is developing cellulose regenerated fiber reinforced technical thermoplastics in a state-funded project with further companies. Since pure natural fibers cannot withstand the high operating temperature of engineering thermoplastics (Ts>230°C), regenerated cellulose fibers are used. These fibers consist of over 99% renewable raw materials. In addition to the ecological aspect, regenerated cellulose fibers are distinguished from conventional fillers such as glass fibers by their lower density and higher impact properties.

Since the engineering plastics PBT are increasingly used in the electronics and automotive sectors due to their high heat resistance and excellent insulating properties, a suitable flame retardant concept is essential. The Department of Polymer Engineering at the University of Kassel has tested various halogen-free flame retardant additives in cellulose and glass fiber reinforced PBT. Flame retardant additives based on phosphorus and nitrogen from Chemische Fabrik Budenheim and Clariant were used. The material starts foaming due to the synergy effect of the two flame retardant additives during ignition. Foaming prevents the material from dripping off and generating flue gas during flame treatment.

Introduction

Polybutylene terephthalate (PBT) is used as neat or fiber reinforced material for applications in electrical and electronic devices and in the automotive sector. Natural fiber reinforced plastics are particularly popular in the automotive industry for interior applications [1].

In previous studies it could be shown that the engineering plastic PBT can also be reinforced with regenerated cellulose fibers [2, 3]. Flame retardancy is an important issue in view of the field of application. In research and development, halogen-free flame retardant systems are at the center of attention. It is assumed that the material combination of aluminum phosphonates (AlPi) and melamine polyphosphat (MPP) do not begin to drip off or smoke gas develops during flame treatment [4–7].

Braun et al. [4] and Töpfer et al. [8] investigated the flame retardancy mechanism of aluminium phosphinate in combination with melamine polyphosphate in glass fiber reinforced polyamide 6.6.

Gallo et al. [9] investigated the flame retardancy of PBT containing aluminium diethylphosphinate and nanometric metal oxides.

The structure property relationships of halogen-free flame retarded PBT and glass fiber reinforced PBT were investigated by Köppl et al. [10].

In this work, the combination of AlPi and MPP are used as flame-retardants for regenerated cellulose reinforced PBT, which act as an intumescent flame retardant system.

Materials

PBT Ultradur B4500 from BASF, Germany with a density of 1.3 g/cm^3 a tensile modulus of 2500 MPa and a tensile strength of 55 MPa and elongation at break of over 50% was reinforced with regenerated cellulose fibers and glass fibers. The regenerated cellulose fibers are from the Company Cordenka, Obernburg Germany. Compared to pure natural fibers, regenerated cellulose fibers have a very high elongation at break of approx. 13%. The regenerated cellulose fibers have a density of 1.5 g/cm^3 a tensile modulus of 2200 MPa and a tensile strength of 825 MPa. Glass fibers (Glass CS 7967) from the company Lanxess, Cologne Germany were used with a density of 2.6 g/cm^3, a tensile modulus of 7300 MPa and a tensile strength of 2600 MPa and elongation at break of 3.5%.

The flame retardant system is made up of two halogen-free additives, aluminum diethylphosphinate (AlPi) and melamine polyphosphate (MPP). AlPi is from the company Clariant, Germany (type Exolit 1230). It is insoluble in water and dose not absorb moisture. MPP is from the Company Chemische Fabrik Budenheim, Germany (type Budit 341). MPP acts as an intumescent flame retardant that expands and foams during exposure.

Table 1: Formulations

Charge:	Matrix:	Fiber:	Flamm retardants:	Abbreviation:
1	PBT			PBT
2	PBT		(AlPi+MPP) 18 wt%	PBT-F
3	PBT	CRF 20 wt%		PBT-20C
4	PBT	CRF 20 wt%	(AlPi+MPP) 18 wt%	PBT-20C-F
5	PBT	GF 20 wt%	(AlPi+MPP) 18 wt%	PBT-20G-F

Processing

The composites were prepared using a twin-screw extruder from the company Leistritz with a screw diameter of 18 mm and a process length of 40 D (ZSE 18 HPE). The PBT was dried below 0.1% moisture content in a vacuum oven at 120°C. The cellulosic fibers were dried at 105°C below 0.5% moister content in an air convection oven before compounding. The PBT granules were fed into the feeding section and the chopped fibers were fed into a side feeder of the compounder by a gravimetric feeding system from Brabender. The initial length of the cellulose fiber was 2 mm and of the glass fibers 4.5 mm. The flame retardant additives are mixed mechanically and dosed undried via the side feeder. A temperature setting below 240°C were used to protect the fibers during manufacturing. Afterwards, the strand was cooled down on a discharger conveyer and pelletized.

Characterization

All composites were conditioned in standard climate (23°C and 50% relative humidity) before characterization for at least 48 h.

The morphology of the materials is characterized by scanning electron microscopy (SEM) MV2300 by CamScan Electron Optics. Fractured notched Charpy samples were sputter coated with gold before examination. Images with high level of magnification (3000x) were taken to obtain an overview of the fiber-matrix properties.

The tensile tests were carried out at a speed of 5 mm min^{-1} on a Zwick Roell Z010 Ulm, Germany according to EN ISO 527. Seven specimens were tested for each material. Young's modulus, the tensile strength, and the elongation at break were evaluated.

Notched Charpy impact tests were carried out on a Zwick Roell with a 4J pendulum according to EN ISO 179-2/1eA. The specimens were notched using a CEAST notching machine. Also, seven specimens were tested for each material. An instrumented pendulum was used to maintain the force curves over the deformation.

Thermal analysis of all materials was performed using a TGA from TA Instruments (TGA 55). The samples were heated from room temperature to 600°C at a heating rate of 10°C min$^{-1,}$ under a constant nitrogen flow of 60 ml min^{-1}. At 600°C the system is switched to oxygen with a flow of 60 ml min^{-1} up to 800°C.

The flammability properties of all investigated formulations were determined by the UL 94 test according to IEC 60695-11-10. In the UL94 a vertical oriented test bar (13mm x 1.6mm x 125mm) was burned with a Bunsen burner for a given time.

Results and Discussion

In Figure 1 the SEM pictures of PBT with 20 wt% cellulose fibers without the flame retardants (a) and PBT with 20 wt% cellulose fibers (b) and 20 wt% glass fibers (c) with flame retardants AlPi and MPP are shown. The fiber matrix adhesion of the sample with glass fibers are significantly higher compared to the other materials a and b. The sample without flame retardants (a) show a smoother matrix surface compared to the flame retardant samples (b,c).

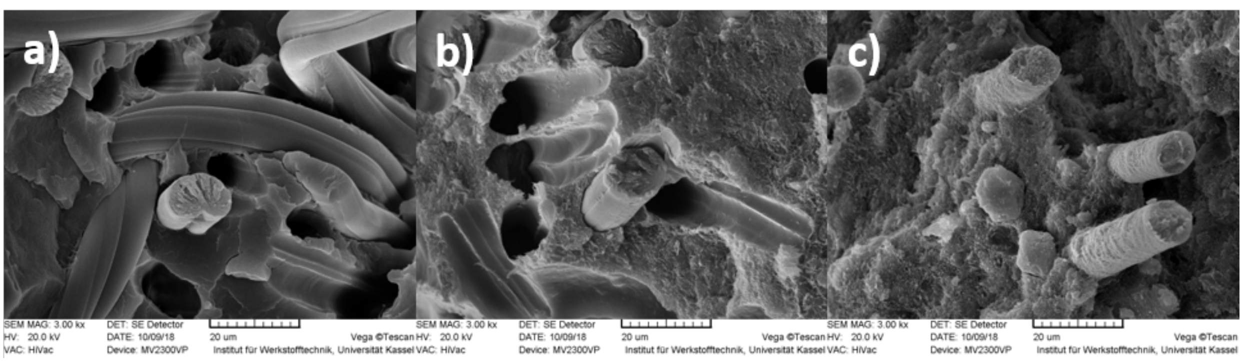

Figure 1: SEM image of a fractured surface a) PBT +20C, b) PBT+20C+F, c) PBT+20G+F

In Figure 2 the mass and mass loss rate of all formulations are shown. The greatest weight loss is between 300°C and 420°C. In this range the decomposition of PBT is 94 wt% > PBT-F 85 wt% > PBT-20C-F 81 wt% > PBT-20G-F 69 wt%. The PBT with cellulose fibers shows a higher mass loss rate between 300-350°C compared to the pure material (PBT), due to the degradation of cellulose fibers. The material with 20 wt% glass fibers show a residue at 800°C of 25.5 wt%. While PBT-F and PBT-20C-F have a residue of 5.5 wt%. It can be assumed that the residue of 5.5 wt% is caused by the flame retardant additives (AlPi and MPP).

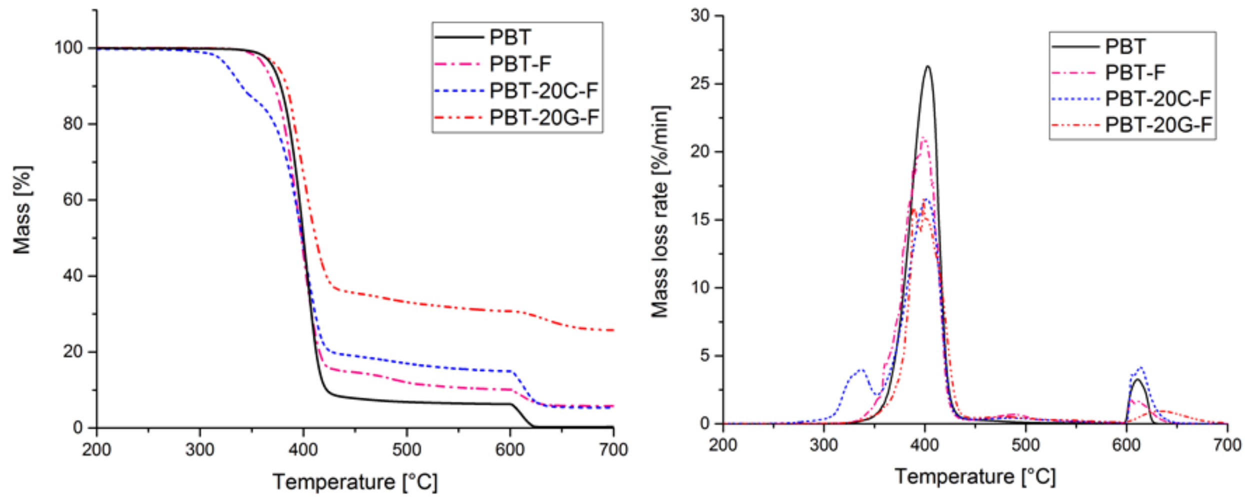

Figure 2: Mass and mass loss rate of all formulations, heating rate 10 °C min^{-1}

The mechanical properties are shown in Figure 3. The Young's modulus increases with increasing filler content. The highest Young's modulus is achieved with the glass fiber reinforced material due to the high stiffness of the glass fibers. With the addition of AlPi and MPP, the notched impact strength of PBT is reduced from 3.9 kJ m^{-2} to 2.6 kJ m^{-2}. The notched impact strength can be improved with a factor of 4 by using 20 wt% of cellulose fibers. The notched impact strength of PBT-20C-F is 9.1 kJ m^{-2}, while the notched impact strength of PBT-20G-F is 3.9 kJ m^{-2}. The tensile strength of PBT can be improved by using cellulose or glass fibers. By using AlPi and MPP the tensile strength is reduced by 20% compared to PBT. With the addition of 20 wt% of cellulose or glass fibers, the tensile strength can be improved by 20% compared to PBT. The elongation of break decreases with increasing filler content. PBT-20G-F has the lowest elongation at break with 1.9%.

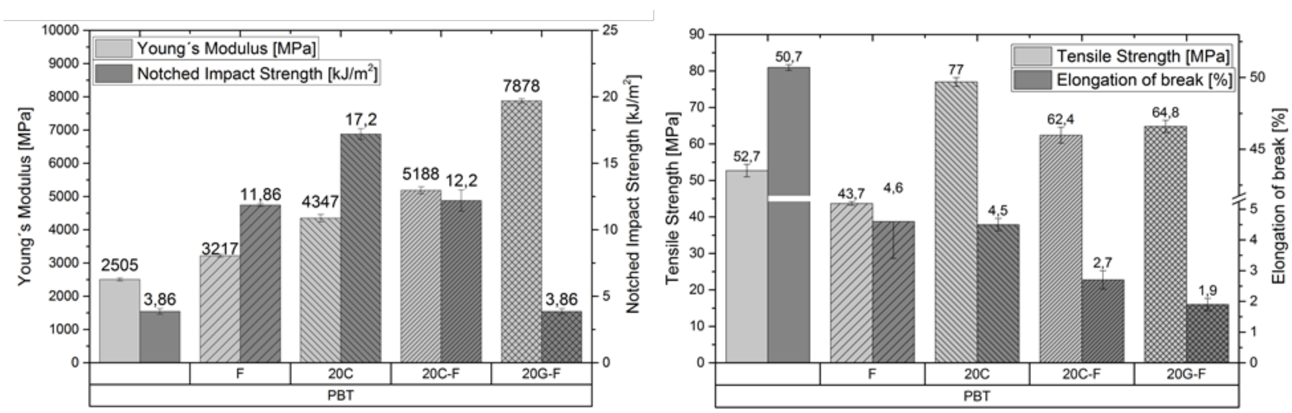

Figure 3: Youngs Modulus, notched impact strength, tensile strength and elongation of break of all formulations

All Materials with the flame retardant combination AlPi and MPP were tested by the UL 94 test with the highest classification V0 (1.5 mm). During the flame treatment the material started to foam up, so there was no dripping off the material.

Conclusion

In this paper the combination of the two flame retardants AlPi and MPP in PBT, natural fiber reinforced PBT and glass fiber reinforced PBT have been described. Furthermore, the mechanical properties were investigated and compared with the materials without flame retardancy.

- After incineration, an inorganic residue of 5.5 wt% remains, which is attributable to the additives AlPi and MPP.
- AlPi and MPP reduces the mechanical properties (except Youngs Modulus). The use of cellulose fibers can prevent the decrease in mechanical properties.
- According to the UL 94 test, a V0 classification can be achieved with 18% AlPi and MPP.

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