DEVELOPMENT OF BIO-BASED AND / OR RECYCLABLE FIBER-REINFORCED, FLAME-RETARDANT POLYMER SYSTEMS

FINAL REPORT

The aim of the present research is the preparation and detailed investigation of fibre-reinforced flame retarded polymer systems, which are derived from renewable resources and/or easily recyclable. These value-added green composites can represent a suitable alternative to the currently applied metal parts, satisfying both the mechanical and flame retardant requirements of the aircraft and transportation industries, while at the end of their life-cycle they can be recycled, thus the amount of the generated waste can also be reduced.

By developing value-added recycling (upcycling) of polymers, their reutilization might be more favoured, instead of their deposit to landfills or the energy recovery. In order to increase the value of secondary raw materials of polyethylene (PE) and poly(ethylene terephthalate) (PET), they were combined, and flame-retarded with conventional FR additives. According to the experiments, the optimal flame retardant composition used as low as 4 wt% of phosphinate-type flame retardant with 1 wt % nanoclay, to ensure self-extinguishing behaviour to the neat PET. The addition of PE to the system increased the dripping of the specimens, thus only V-2 rating in the UL-94 test could be reached. The systematic study on different potential synergists showed that the high processing temperature of PET prohibits their application, as the FRs already degrade at that temperature. The mechanical properties (e.g. flexural strength and modulus) of flame retarded PET system showed comparable, or in some cases even higher values than that of conventional raw materials used e.g. as TV parts [1].

Biodegradable biopolymer based systems have been developed in order to prevent the use of non-renewable resources, and to minimize the waste-formation, according to the principles of green chemistry. In flame retarded form, these systems decrease the risk of fire. After the first attempts with poly(hydoxy-butirate), due to its very low melt-viscosity, and high price, we draw our attention to the more economical and easily processable poly (butylene-succinate) (PBS). Several intumescent-type phosphorus flame retardants (ammonium polyphosphate, APP) were tested together with DOPO (9-oxa-10-phosphaphenanthrene-10-oxide) and its derivatives to find an appropriate composition for PBS: two types of unmodified APP (APP1 and APP2), an APP optimized for polyolefins (APP3) and a microencapsulated APP (APP4); while DOPO was used alone, and in salt forms: ammonium-salt (DOPO_A) and melamine-salt (DOPO_M). The samples were subjected to small-scale thermal and flammability tests to determine the most effective composition. Based on the calorimetric results, the intumescent-type flame retardants were more effective, as they could significantly reduce the heat release. The oxygen index values (LOI) of the APP-containing samples fall in the range of 26-31 V/V%, however, in UL-94 tests they reached only V-2 rating due to the flaming droplets during burning. Contrarily, the samples flame retarded with DOPO-additives didn’t reduce the heat release of the samples, but in UL-94 tests V-0 rating was reached with only 5 wt% of additive, while the LOI values were higher than 40 V/V%. This contradiction can be explained by the mode of action of the different FRs: The intumescent flame retardants act in the solid phase by char formation and insulation; while the DOPO-based flame retardants act in the gas-phase by radical scavenging mechanism, as proven by the LP-FTIR measurements. The best performing APP3 and DOPO_A samples were further analysed by means of tensile and falling weight impact tests. The results showed that although the DOPO_A reduces strength of the polymer, the APP3 sample has comparable mechanical properties to that of the reference PBS.

The severe dripping of the polymer, which caused the V-2 rating of APP-containing PBS samples were effectively prevented in poly(lactic acid) (PLA) system, by using nanoclays as synergistic additives [2]. The platelet-like montmorillonite and the fibre-like sepiolite were used both in unmodified and organofilized form. The results showed that the maximum applicable amount of the nanoclays is 1.5 wt%; at that level V-0 rating was reached, as the flaming droplets were eliminated through the increased melt viscosity of the PLA.

A thermosetting bioepoxy resin has been synthesized from citric acid as renewable starting material [3]. The flammability of bioepoxy resin was studied using several types of phosphorus-containing flame retardants including different inorganic-, or alkyl- and aryl phosphates, phosphonic acid salts and red phosphorus-based flame retardants, have been applied in two different (a high-viscosity and a water-borne) sorbitol-based bioepoxy resins in different concentrations. The effect of the flame retardants on the thermal (thermogravimetry), thermomechanical (DMA) and flame retardant properties was studied. According to the results, the shorter-chain aliphatic P-esters had lower effect on the glass transition temperature and on the thermomechanical properties, mainly because of their higher P-content and consequently lower amount needed. All flame retardants delayed the thermal degradation of the matrices, and higher amount of char was received in all cases than in the case of the reference systems. The FRs acting mainly in the condensed phase were more effective in the horizontal UL-94 tests and mass loss type cone calorimeter tests, while FRs having gas-phase effect could increase the LOI value of the samples more considerably. However, to reach V-0 in the vertical UL-94 test, only those FRs were effective, which show both intumescent- and gas-phase effect. Comparing the efficacy of the different FRs in high-viscosity and water-borne epoxy resins, it can be concluded that similar results can be reached, but the water-borne resin itself has lower flammability, so the relative increase in the FR properties is worse in that case [4,5].

By changing the curing agent, a fully water-borne bioepoxy system was received and flame retarded by the addition of some phosphorous based FRs. The self-extinguishing behaviour was observed at 3%P for all the investigated FRs and 1%P in the case of APP, while LOI values were practically good for all FRs and extremely improved in the case of APP (as high as 48V/V% at 3% P-content). Mass loss calorimetry measurements have proved the effect of all the used FRs on SPE epoxy resins under simulated fire conditions. The residual char yields for phosphonate polyol and alkyl phosphate blends were lower than in the case of aluminum tris-(diethylphosphinate) (AlPi) samples, however, AlPi samples showed higher total heat release (THR) and peak heat release rate (pHRR), due to the insufficient barrier effect of the formed char leading to more decomposition of the underlying material. APP sample at 3%P content showed the best results as THR decreased by 43% and pHHR decreased by 65% with more elongated burning compared to the reference SPE matrix. The efficient intumescent effect of APP provides a good explanation for its superior flame-retardant effect [6]. In order to improve the charring ability of AlPi, it was combined with melamine-cyanurate (MC). The total loading of AlPi was kept at 4.5 %, and the effect of using 5% and 10% loadings of MC was investigated. It was proven that the incorporation of these P and N-containing FRs together could better enhance the flame retardancy of the fully waterborne epoxy system compared to the cases of using only one of them. In cone calorimeter tests, no enhanced barrier characteristics were observed by increasing MC content in the presence of AlPi. This effect can be observed also in flammability tests. The lower stability of residue by increasing MC content might also explain why the best results were observed in case of MC (5%) + AlPi (1%P) sample as the self-extinguishing rating V-0 was permitted with relatively good LOI. [7].

Flame retarded epoxy resin composites reinforced with carbon fibres produced from renewable resources, have been developed for safe transportation [8]. Furthermore, we studied the effect of a multilevel presence of carbon-based reinforcements—a combination of conventional load-bearing unidirectional carbon fibre (CF) with multiwalled carbon nanotubes (CNT) and conductive CNT-containing nonwoven carbon nanofabric (CNF(CNT))—on the fire performance, thermal conductivity, and mechanical properties of reference and flame-retarded epoxy resin (EP) composites. The inclusion of carbon fibres and flame retardant reduced the peak heat release rate (pHRR) of the epoxy resins. The extent to which the nanoreinforcements reduced the pHRR depended on their influence on thermal conductivity. Specifically, a high thermal conductivity is advantageous at the early stages of degradation, but after ignition it may lead to more intensive degradation and a higher pHRR; this was seen especially in the reference samples without flame retardant. The lowest pHRR (130 kW/m2) and self-extinguishing V-0 UL-94 rating was achieved in the flame-retarded composite containing all three levels of carbon reinforcement (EP + CNF(CNT) + CNT + CF FR). The plasticizing effect of the liquid flame retardant impaired both the tensile and flexural properties; however, it significantly enhanced the impact resistance of the epoxy resin and its composites [9].

Biocomposites can be prepared by using natural fibres in thermoplastic or thermosetting materials. In order to be able to develop a biocomposite, which might replace the currently used-carbon-or glass-fibre reinforced composites, the strength of the different fabrics was determined by means of strip tensile tests and ball burst procedure. Several different fabrics were tested: jute, hemp and linen with different areal weight and weave. The chemical composition of the fabrics was characterized by ATR-IR spectrometry. As for the easier processing, the manufacturers often use synthetic subsidiary fibres. The identification allowed us to select the fully natural fabric for further investigations.

The effect of the fibre length and orientation on the flammability of an epoxy resin was evaluated by means of cone calorimetry. For this purpose, chopped flax fibres and woven fabrics were compared at the same level of fibre content (20 wt%). The same FR treatment allowed higher reduction in the heat release in the case of the woven fabrics, i.e. the total heat release was reduced by 30% when the fabrics were used, while this reduction was only 25% with the use of short fibres.

New, reactive fibre-treating agents were synthesized from the reaction products of absolute ethanol and phosphorus-pentoxide. The reaction meets the requirements of the green chemistry, as no additional solvent is used, and there is no side-product formation, as the phosphorus-pentoxide reacts with the ethanol in an addition reaction. The products are mono- and diethyl ester of phosphoric acid in 2:3 mole ratio. These molecules were then reacted with a silane compound having isocyanate function, via their phosphoric acidic –OH groups. The formation of the product (PSi) was followed by FTIR spectroscopy, where the continuous decrease and final elimination of the peak related to the isocyanate functional group (2283 cm-1) was accompanied with the appearance of the peaks related to the carbamate group (3334 cm-1: carbamate N-H, 1721 cm-1: carbamate C=O and 1536 cm-1: carbamate C-N). Then cellulose was modified via its –OH groups with the prepared P-containing silane, resulting in reactively flame retarded natural fibres. The optimal reaction circumstances for the reparation of P-cellulose were identified based on the results of TGA measurements. In the first step, the ratio of cellulose and the silane compound were changed from 1:0.5 to 1:1.25 (cellulose:PSi). According to the results, the optimal ratio of the two components was 1:1; the beginning of the degradation decreased moderately compared to the neat cellulose, and the amount of the charred residue increased up to 38%. The concentration of the treating suspension (the fibres are suspended in the solution of the P-silane) has also a significant influence on the effectiveness of the treatment: in more dilute suspensions more silane can be bound to the cellulose within the same reaction time. However, the use of very dilute suspensions is not suitable in bigger quantities, thus as an optimal concentration, 1 g cellulose was dispersed in 200 ml toluene. The neat and modified cellulose fibres were then incorporated to PP matrix at 10 w/w% loading. According to the results, the thermal stability of the system decreased with the incorporation of P-cellulose, as the degradation of the P-compounds start at lower temperature. During the mass loss type cone calorimeter tests, it revealed that the incorporation of the P to the cellulose is beneficial. When unmodified cellulose was added to the PP the peak of heat release rate slightly increased, which could be avoided by the P-treatment of the fibres. The total heat released could be decreased by around 10% with the use of P-cellulose, and around 5% charred residue was observed after the test, while the references (neat PP and 10% unmodified cellulose-containing PP) burned completely.

In the case of biocomposites based on the thermoplastic poly(lactic acid) (PLA), instead of the halogen-containing flame retardants, which are poisonous, and harmful for the environment, “green”, phosphorus-containing intumescent multifunctional additives were combined with reinforcing fabrics in order to reduce the additive content. Flame retardant fibre treatment methods have been elaborated. During the treatments, plant fibres were immersed in aqueous solutions of diammonium phosphate (DAP) and urea (U). In order to clarify the composition-structure – effect relationship, and the fibre – matrix adhesion, distribution of phosphorus containing compounds between the phases of FR-flax-fabric reinforced micro-encapsulated intumescent flame retardant (IFR) containing PLA composites were analysed systematically. The achieved improved mechanical and fire safety performance is explained by the better interfacial interaction provided by the phosphates being present both in fibre and matrix phase in a well-balanced distribution [10].

Cyclodextrin (CD) microfibres have been firstly applied in the flame retardancy of poly(lactic acid) [11,12]. The CDs were used in powdered and in fibrous form, and also they were modified with the above-described PSi It is demonstrated that the efficiency of an intumescent flame -retardant system can be noticeably improved just by reducing the particle size and aspect ratio of the used charring agent. The high-surface-area CD microfibres were found to have better char promoting performance in intumescent flame-retarded PLA system than the conventional CD powder. By increasing the specific surface area of the used charring agent, a remarkable increment of the LOI value (from 28 V/V% to 31 V/V%) and the PSi surface treatment further increased these values (to 32 V/V% and 37 V/V%, respectively).

Polyurethane (PUR) is a suitable material as charring and foaming agent in the intumescent flame retardants, thus phosphorus-containing PUR systems have also been developed. After their life-cycle, from the waste polyurethane, a new, environmentally benign flame retardant can be prepared [13,14]. The synthesis of the modified PUR monomer was followed by *in-line* FTIR and Raman spectrometry. By following the reaction, the formation of the non-desired side-products, which could hinder the polymerization reaction, could be avoided.

A new, bioepoxy resin-microencapsulated intumescent flame retardant system was synthesized using sorbitol-based bioepoxy and unmodified ammonium polyphosphate. This new microcapsules were used in PLA [15] and in PP [16,17]. Through the increasing shell-thickness, the microcapsules could effectively decrease the flammability of PLA. In this system, the resin:APP 2:10 ratio was found to be optimal, as it provided excellent flame retardancy (UL-94 V-0 rating, LOI value of 29, and heat release reduction of almost 40%), together with acceptable tensile strength. In polypropylene, the shell-thickness of the microcapsules were further increase, as PP due to the lack of hydroxyl functional groups has no charring ability at all. By increasing the ratio of resin:APP to 5:10, significantly higher amount of charring agent could be incorporated to the PP matrix, which resulted in V-0 rating, and as high as 36 V/V% LOI value. As control experiment, the physical mixture of unmodified APP and grinded bioepoxy resin was also added to PP with the same mass composition as the corresponding microcapsules. In this case, although also the physical mixture reached the self-extinguishing V-0 rating in UL-94 test, the LOI values were significantly (by 8-9 V/V%) lower than that of the results of the corresponding microcapsule-containing samples. The difference was also conspicuous in the mass loss cone calorimetry tests: the peaks of heat release rate were higher, and they appeared by 100 sec earlier in the case of the samples containing the physical mixture of APP and bioresin. This difference can be attributed by the dispersion of the components of the intumescent system: in the case of the microcapsules, the acid-source APP is covered by the charring agent (bioresin shell); while in the case of the physical mixture they have to find each other to form the protective char layer on the surface of the polymer.

In order to be able to continuously *in-line* investigate the distribution of the additives, which were proven to be important according to the structure-effect relationship, a widely applicable image analysis method has been developed [18]. As the distribution of the components is predominantly influenced by the dosing technology, in order to able to control it, a new method based on image analysis has been developed, which can be prosperously applied in several types of technologies (e.g. in the pharmaceutical industry) [19]. Based on the image-analysis, a possible PAT (process analytical technologies) tool was developed by the continuous recording and automated analysis of the images (machine vision) with a feedback possibility to ensure proper distribution of the low-dose additives [20]. For better understanding the processes during mixing, the digital twin model of continuous blending was developed using artificial neural networks. As the long residence time of a water-sensitive polymer (e.g. PET or PBS) in a high-temperature equipment may cause hydrolytic degradation even when dried FRs are used, the residence-time distribution models were also taken into account [21].

The alterations in the properties related to the crystallinity of polymer fibres, resulting from changes in the environmental parameters (e.g. hydrolytic circumstances, thermal annealing, solvent) have been studied by thermal [22] and *in-line* spectroscopic methods [23]. SEM images revealed a dramatic relaxation of the samples treated at 85 °C; on the other hand, ethanol-treated fibres mostly preserved their original shape. The fibre diameters were in the range of 0.25–8.5 μm and were found to increase by 0.3 and 0.6 μm as a result of solvent and heat treatment, respectively. Conventional DSC showed that solvent-induced crystallization progresses 2–3 times more rapidly; besides, the large surface-area-to-volume ratio further increases the efficiency of the methods. Differentiation between the melting of α′ form and recrystallization to α form within a single sample was accomplished using the temperature-modulated DSC method. As this effect was absent from the MDSC curves of ethanol-treated fibres, it was evinced that this technique exclusively induces the formation of the more stable α polymorph. Raman microspectroscopy mapping and XRD measurements confirmed this phenomenon, allowing *in-line* observation of the shift between α and α′ crystalline structure. As the crystallinity is one of the most important parameters, a separate reactor has been developed to carry out effective crystallization procedures, which can be applied on several fields of the industry [24].

As light-weight materials, the polymer foams can also be used in several fields of the industry. *In-line* spectroscopic analytic method has been developed for the control of the preparation of foamed PLA structures for the automotive industry, which allows reducing the energy-consumption [25]. This method is suitable for the quality assurance of the production of flame retarded PLA foams as well [26].

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