Budapest University of Technology and Economics
Faculty of Chemical Technology and Biotechnology

PLASTIC RECYCLING ASSISTED BY SPECTROMETRY

Theses of Ph.D. dissertation

Submitted by:
Brigitta Bodzay

Supervisors:

István Csontos
senior lecturer

György Marosi
professor

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1. INTRODUCTION

Hungary, as a consequence of joining to the European Union (EU), assumed to follow the directives and fulfil the requirements of EU, for saving the Earth's resources. In order to close the lifecycle loop and to decrease the loading of the landfills, dealing with wastes became the responsibility of the producers. Therefore the development of recycling technologies is nowadays a relevant challenge.

Hungary adopted the 2000/53/EC directive of EU in law (267/2004. (IX. 23.)) dealing with handling of end-of-life vehicles. This regulation determines numbers and deadlines. From 01.01.2006 85 % of the vehicles has to be recycled; 80 % for material and 5 % for energy recovery. These numbers changes from 01.01.2015; 95 % of the vehicles has to be recycled; 85 % for material and 10 % for energy production.

Taking into consideration the tendencies in the future; the weight of the vehicles and the ratio of used plastics (currently 11 %) will be increased, causing 31.000 t plastic wastes per year in Hungary just from this sector. The development in polymers recycling for material or energy production is necessary. Almost the half of the plastics (41 %) used in a vehicles is polypropylene, therefore this PhD work focuses on the recycling of polypropylene originated from automotive wastes.

The objective of this PhD work is to develop a possible way for upgrading polypropylene wastes originated from end-of-life vehicles.

In order to recover polypropylene, separation and analysis the composition of mixed plastic waste is necessary, which is complicated with the widely used analytical devices; therefore a development of a new method (LP-FTIR) became necessary to obtain information also about the black particles. On the one hand our aim was to verify its applicability on investigation of waste and filled polymers; on the other hand to develop a complex waste investigation protocol that promotes the recovery of quite pure polymers based on density separation limits.

The polypropylene with low filler content separated by density is intended to upgrade with flame retardancy besides unchanged or enhanced mechanical properties, to adapt it for automotive applications. Our further aim was to explore the effect of fillers on the flammability.

It was recognized that the mixed waste of high polypropylene and filler content is adequate carbon source for formation of nano and micro sized carbon fibres/tubes by application of LP-FTIR technique. Model experiments were set up based on neat polymers in order to define the required materials and conditions.

2. MATERIALS AND METHODS

Neat polypropylene (PP - Moplen HP 400 H®) was used during the development and parameter settings of (LP)-FTIR coupled method. The comparison of this new method to FTIR spectrometer coupled mass loss type cone calorimeter (MLC-FTIR) was performed based on poly(vinyl chloride) (PVC - Grabiol Stop JSK®). The effect of different additives magnesium- (MH - Magnifin H5MV®), and aluminium-hydroxide (ATH - ALOLT 60 DLS®), and melamine borate (MB – self prepared) in ethylene vinyl acetate (EVA- Ibucell K 100®) matrix was investigated, furthermore mineral clays (OMMT - Bentone SD-1®), (SEP – Pangel S 9®) in polypropylene matrix (PP - Moplen HP 400 H®) in presence and in absence of magnesium hydroxide (MH - Magnifin H5MV®) and maleic anhydride grafted polypropylene (MA-g-PP - Licomont AR504®). The effect of mineral clays on the decomposition and on the char structure was studied in styrene acrylate copolymer (SA - Plioway ECT®, Pliolite Ultra 100®), and in SA based flame retarded paint (Polylack®). Influence of copper salicyl aldehyde (CuSA) was investigated on the decomposition of intumescent flame retardant containing (IFR) polyethylene (PE) compounds obtained from University of Lancashire (PE, PE-IFR, PE-IFR-CuSA).

The application of the developed complex waste investigation protocol was demonstrated on automotive shredder wastes separated into density fractions in the range of 0.88-1 g/cm^3 with 0.01 g/cm^3 steps, and in the range of 1-1.3 g/cm^3 with 0.05 g/cm^3 steps.

In order to upgrade the polypropylene with low filler content stabilizer (Irganox B125®), ammonium polyphosphate (APP –Exolit AP766®) flame retardant, and glass fibre (GF - DS 2200-13P®) reinforcement were used.

For preparation a multilayer reinforced composite, a neat polypropylene (PP - Tipplen H 119 F®), and a secondary polypropylene (ρ<0.92 g/cm^3) was used with intumescent flame retardant additive system (APP – Exolit AP 422, pentaerythritol – PER, ground polyurethane waste - RecPUR), glycerol monostearate (GMS) as a compatibilizer, and glass fibre (GF-DS 2200-13P) as a reinforcement were applied. For modelling synthesis of carbon nanotubes and carbon nanofibers made of high filler containing secondary polypropylene (1.1< ρ <1.3 g/cm^3) neat PP (Moplen 500 N®), PE (Quamar CD18N®), PP/PE copolymer (Moplen EP 340S®) and different types of mineral clays (MMT – Microtec®, Fe-MMT – Türkös®, OMMT K1 – self prepared OMMT – Bentone SD-1®, SEP – Pangel S 9®) were used.

The analysis of the plastic waste fractions were performed by FTIR (Bruker Tensor 37) and Raman (Horiba Jobin-Yvon LabRAM) spectrometer, by LP-FTIR coupled method and the filler content was determined by heating the waste under conditions of cone calorimeter. The purity of each fraction and the oxidative induction time (OIT) were investigated by DSC (Setaram DSC 92), to determine the melt flow index (MFI) Ceast Modular Melt Flow 7027.000 device was applied.

The polymer composites were prepared in a Brabender Plasti Corder PL 2000 type internal melt mixer, and then pressed with Collin P 200 E type stamp. The flammability was investigated using UL-94, limited oxygen index (LOI) and mass loss type cone calorimeter (FTT Technology). The mechanical tests were carried on Zwick Z020 universal tester.

For identification of carbon nanotubes and carbon nanofibres TEM (FEI Morgagni 268D), SEM (JEOL JSM-6380LA) Raman, and thermogravimetric (TG - SETARAM Labsys TG) measurements were performed.

3. NEW SCIENTIFIC RESULTS

3.1 A new coupled analytical method (laser-pyrolysis (LP)-FTIR Spectrometer) has been developed, and the effect of its working conditions (laser power, sampling method, atmosphere, time of exposure) has been determined. With this new „in-line" method, together with other components, also the chlorine content of the plastic wastes can be detected in real time with high sensibility. It was verified by LP-FTIR and ATR methods, that the acetic acid evolved during the decomposition of EVA copolymer was adsorbed by metal hydroxide additives. Modelling of the pyrolysis (dark flame zone, between the polymer and the flame), of flame retarded polypropylene the mode of action of synergistic flame retardant components (mineral clays, copper salicylic aldehyde) was clarified. [I]

3.2 A complex, multicomponent waste investigation protocol was developed at first in order to characterise and analyse the composition of plastic wastes. The challenge of the identification of black particles can be answered by the application of LP-FTIR, because the ratio and the quality of evolved gases act as a fingerprint of the polymer. The application of the protocol was verified on automotive wastes. Based on the analysis of polymers originated from end-of-life vehicles it was concluded that well performed density separation results in the recovery of the following polymers; $\rho<0.92$ g/cm^3 polypropylene, $0.94 < \rho < 0.97$ g/cm^3 polyethylene, which are suitable for reprocessing. In the range of $0.92 < \rho < 0.94$ g/cm^3 mixed polyethylene and polypropylene was found, and between 0.97 < ρ < 1.1 g/cm^3 styrene containing polymers (PS, ABS, SBS, SIBS, SAN) are dominant. It was established, that even the quite pure PP fraction contains inorganic additives around 1 % (CaCO3, talc and mineral clay). [II-V]

3.3 It was confirmed, that the upgrading of secondary polypropylene with flame retardant additives is feasible, and because of the filler content of polymer wastes, the flame retardant properties differ from the neat polymer. It was verified that the low (<1%) filler content of the polymer wastes (mineral clays) influences the rheological properties, thermo and thermo oxidative degradation. When the flame retardant concentration is low these fillers increase the stability of the charred foam, while at high concentration of flame retardant additive it makes the charred foam too rigid. As a result of anti-dripping (viscosity enhancing) effect of the small amount of filler, the V-1 classification according to UL-94 standard can be reached by unexpectedly low concentration of flame retardant. This advantageous effect can not prevail under the condition of limited oxygen index, which became lower. [VI-IX]

3.4 A new method was elaborated to realize simultaneous improvement in the flame retardancy and reinforcement of polypropylene waste. In presence of flame retardants, the reinforcement effect of glass fibre can not be realized; therefore with modification of composite structure (but maintaining the composition) enhancement was noticed both in flame retardancy and tensile strength. A mutilayer composite was developed, which contains 65.5 % of recycled polymer, where the core is reinforced with glass fibre covered by flame retarded shell layers. Enhanced flame retardancy (5 min longer time to escape) was achieved using this layered composite compared to the mixed composite with the same composition, therefore the time to escape could be extended only with modification of the composite structure. [X- XV]

3.5 It was recognized, that without any metal catalyst multiwall carbon nanotubes (MWCNT) and carbon nanofibres (CNF) can be produced from polypropylene containing waste by application of LP-FTIR. This method can be realized simpler than the carbon nanotube and carbon nanofibre synthesis methods well-known from the literature, and makes the utilization of high filler containing polypropylene (PP) waste possible (which is not feasible in the form of secondary polymer). Systematic model investigations allowed the determination of the influence of the parameters (type of mineral clay, its iron content and gas barrier properties, PP content, laser irradiation time and applied atmosphere). Correspondence was observed between the composition of the evolved gases and carbon nanotube/fibre formation thus the composition of the gas could be used as marker of the formation of carbon objects. It was concluded that the iron content, the shape and the adequate dispersion of the mineral clay is necessary. After pyrolysis of 5 % organophilic montmorillonite containing polypropylene at 7.5 W for 1 min in closed cell the best yield was achieved. [XII, XIII, XVI]

4. APPLICATION OF NEW SCIENTIFIC RESULTS IN PRACTICE

Based on the density separation limits determined in the frame of this PhD work the polypolefins, originated from the plastic stream of car shredder, can be recovered. With application of polypropylene obtained from car shredder ($\rho<0.92$) mixed with flame retardant additive and glass fibre a layered composite was produced for automotive applications. To demonstrate the applicability of waste a car door opener was designed and produced by injection moulding using PE waste with stabilizer and glass fibre reinforcement.

With applications of polypropylene waste and secondary polyurethane from car seats, as a flame retardant additive, a self-extinguishing geomembrane prototype for landfill applications was produced, which contains 50 % of secondary polymers. The polypropylene waste with high filler content, seemed previously valueless, is adequate carbon source for formation of nano and micro sized carbon fibres/tubes by application of LP-FTIR technique, which can be used in the upgrading as a reinforcing and flame retardant additive. [IV, V, XV, XVI]

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