

Fire retardancy and environmental assessment of rubbery blends of recycled polymers

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Abstract. Flame retarded thermoplastic polymer compounds were prepared containing recycled rubber tyres, low density polyethylene, ethylene vinyl acetate copolymer and an intumescent additive system consisting of waste polyurethane foam and ammonium polyphosphate. The effect of the additives on the combustion properties was characterised by Limiting Oxygen Index, UL 94 and mass loss calorimetric measurements. The environmental impact was estimated by determining the gas components of CO₂ and CO evolving from the compounds during the burning process using a gas analyser system constructed by coupling an FTIR unit to a mass loss calorimeter. The new material forms a thermoplastic rubber of excellent processability making it suitable for application in construction industry.

Keywords: recycling, rubber waste, intumescent flame retardant, evolved gas analysis, polyurethane

1. Introduction

There are over 2.5 million tonnes of waste tyres arising in Europe each year. This high amount initiated the commencement of the 2000/53/EC directive of the European Parliament and of the Council [1], which prescribes the recovery, reuse and recycling of the end-of life vehicles including rubber tyres. Since July 2006, waste tyres have been totally banned from landfills.

Utilizing options of waste rubber vulcanizates are incineration, pyrolysis [2, 3], gasification [4–6], devulcanization (e.g. chemical [7], mechanochemical [8, 9], supercritical [10, 11], ultrasonic [12, 13]), or blending either in thermoset [14–16] or in thermoplastic [17–19] polymer matrices. In this work we selected the last mentioned option combining it with upgrading that is to transform the rubber waste containing compound to a special flame retardant material.

There are known many ways to obtain flame retardant rubbers (synthetic or natural) or rubber containing composites by incorporation of flame retardant additive. E.g. ammonium polyphosphate/aluminium trihydroxide system [20], ammonium polyphosphate [21], ethylene-diamine phosphate [21] or nanoparticles (e.g. nanoclays [22], nano-calcium sulphate [23], nano-magnesium hydroxide [24–26]) are suitable flame retardants.

In our work we used ammonium polyphosphate/polyurethane intumescent additive system. This system proved to be an effective flame retardant in ethylene propylene rubber [27], polypropylene [28] and ethylene vinyl acetate copolymer matrices [29, 30]. Bugajny *et al.* pointed out that the chemical reaction taking place between ammonium polyphosphate and thermoplastic polyurethane leads to the formation of an intumescent shield and provides improved thermal stability for the material [31].

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Carbon dioxide/carbon monoxide yield ratio and toxicity of fires can be evaluated from small scale tests such as cone calorimeter or tube furnace (Purser furnace) methods [32, 33]. However the results obtained from these tests may differ because of the varying test conditions (e.g. vitiated combustion, rapid quenching of the fire gases, less- or well-ventilated conditions etc).

This work focuses on the flame retardant effect of APP/PU intumescent additive system in LDPE/EVA based polymer matrix containing rubber waste, and on the environmental effect of the additive by analysing the evolved gases during combustion. The flammability was tested by LOI, UL 94 and mass loss calorimeter and the gas analysis was performed by FTIR attached in line to the mass loss calorimeter.

2. Experimental

2.1. Materials

Low density polyethylene (LDPE): Tipolen AE 2016 (TVK Rt. Hungary). *Ethylene vinyl acetate copolymer (EVA)*: Ibusell K-100 (H. B. Fuller, Germany). *Recycled rubber (RUB)*: the 200–600 μm fraction of a rubber powder prepared by an ultra high pressure water jet cutting process [34] (Regum Kft. Hungary). *Ammonium polyphosphate (APP)*: Exolit AP 422

(Clariant Ltd. Germany). *Recycled polyurethane foam (PU)*: ground, freon free waste polyurethane foam recovered from fridges (Amatech-Polycel Inc. Germany). *Glycerol monostearate (GMS)*: commercial product (Chemiplast Kft. Hungary).

2.2. Preparation of samples

Compounding: the components were homogenised in a Brabender Plasti Corder PL 2000 apparatus, at 150°C, with a rotor speed of 50 rpm, for 10 min.

Test sheets: the blends were compressed in a Collin P 200 E laboratory compression moulding machine at 150°C, with 10 bar, for 10 min.

2.3. Methods of evaluation

UL 94 flammability and Limiting Oxygen Index (LOI) according to the standards [35, 36]. *Mass loss calorimetry* with heat flux of 50 kW (this value corresponds to the heat generated in a well-developed fire [38]), without direct ignition according to the standard [37]. *Infrared gas analysis (FTIR)*: the gas evolving from the samples being exposed to 50 kW/m² radiation in the mass loss calorimeter was analysed by a Bruker Tensor 37 FTIR. The mass loss calorimeter was connected (at atmospheric pressure) with the infrared spectrometer according to Figure 1, by interface elements con-

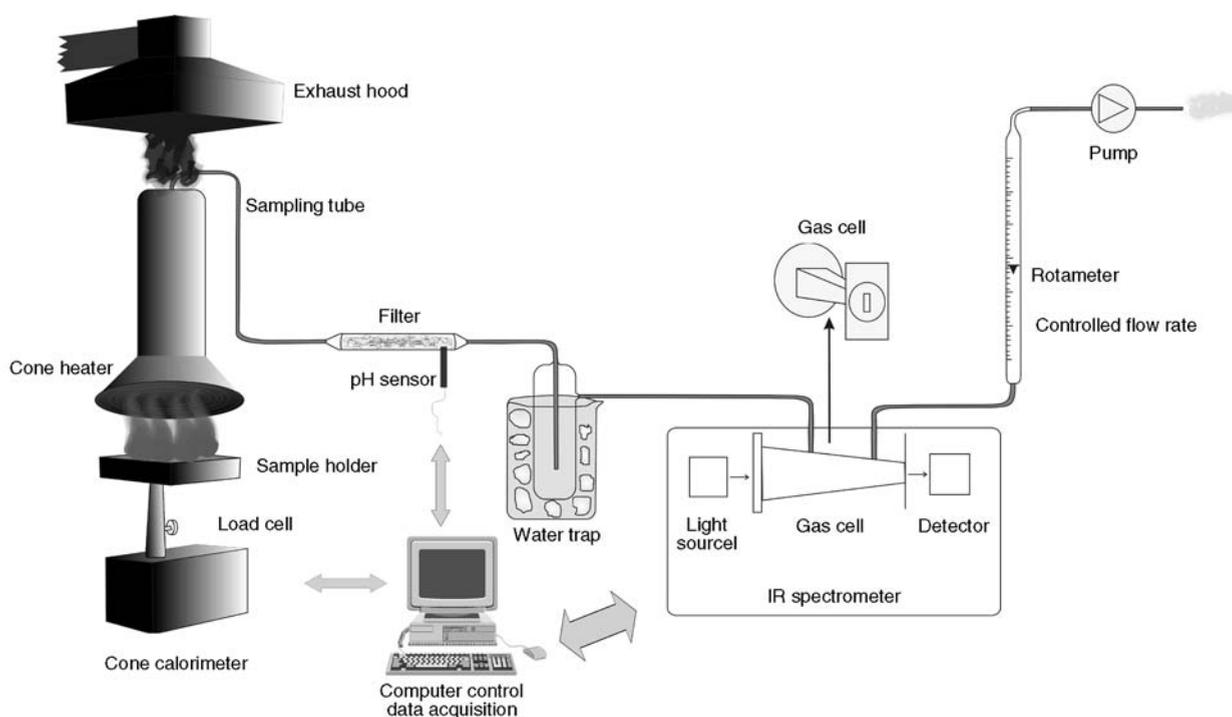


Figure 1. Scheme of gas analyzer consisting of the mass loss calorimeter, FTIR spectrometer and interface elements

sisting of glass sampling tube, glass-wool filled filter and condenser, in order to detect the evolved gases. The pathlength of the single pass gas cell was 100 mm made of stainless steel. As the gas cell contains a NaCl window, which is sensitive to water, the evolved water vapour was condensed in a trap cooled by the mixture of water and ice. The spectra recorded throughout the test were evaluated by Opus 5.5 software in the range of 650–4000 cm⁻¹. Among the toxic products we focused on CO and CO₂ with characteristic bands at (2171 and 2118 cm⁻¹) and (2363, 2341 and 2336 cm⁻¹) and identified by using Reference [39].

Mechanical properties: tensile properties (tensile strength, relative elongation at break and tensile modulus) were measured according to the standard [40] by a Zwick Z020 testing machine. The measurements were evaluated by TestXpert V10.11 software.

3. Results and discussion

3.1. Flammability

The compositions of the Reference, of the compounds containing APP/PU intumescent additive system (Samples 1–3) and of the compound con-

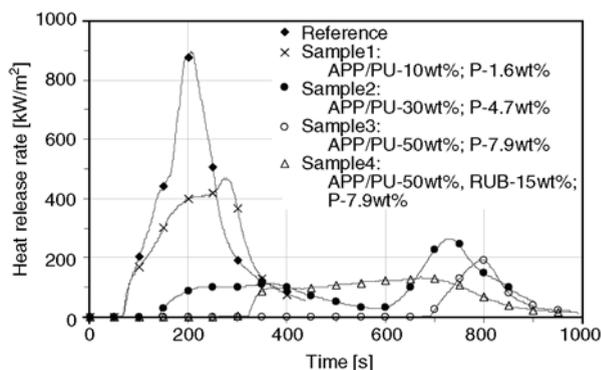


Figure 2. Heat release rate (HRR) vs. Time in mass loss calorimetric measurement of the compounds

taining APP/PU/RUB additive system (Sample 4) are given in Table 1. The APP/PU weight ratio was 1/1 in all cases. The LDPE/EVA weight ratio was also constant in all samples. Table 1 contains also the results of UL 94 and LOI flammability tests and the characteristic values could be evaluated from the Heat release rate (Figure 2) and Mass loss curves (Figure 3) of mass loss calorimetric measurements.

Comparing the characteristics of Reference and Sample 1, it can be seen that phosphorus content of 1.6 wt% does not lead to improvement in either UL 94 grade, LOI or *t_{ign}*. Both Reference and Sam-

Table 1. Composition in wt% and flame-retardant characteristics of Reference and Sample 1, 2, 3 and 4

Components	Reference	1	2	3	4
LDPE	26.6	23.9	18.5	13.1	9.1
EVA	72.4	65.1	50.5	35.9	24.9
APP	–	5.0	15.0	25.0	25.0
PU	–	5.0	15.0	25.0	25.0
RUB	–	–	–	–	15.0
GMS	1.0	1.0	1.0	1.0	1.0
Total	100.0	100.0	100.0	100.0	100.0
Characteristics					
Phosphorus content [wt%]	0.0	1.6	4.7	7.9	7.9
UL 94 measurement					
Horizontal burning					
Flame velocity [mm/min]	37.2 ± 2.8	35.0 ± 1.0	extinguish	extinguish	extinguish
Dripping	yes	yes	no	no	no
Vertical burning					
Dripping	yes	yes	yes	no	no
Grade	H-B	H-B	V-2	V-0	V-0
LOI, (V/V) [%]	22	22	26	30	29
Mass loss calorimetric measurement					
Time to ignition (<i>t_{ign}</i>) [s]	70	70	140	695	325
Peak of Heat Release Rate (HRR _{max}) [kW/m ²]	900	475	275	190	135
Time to HRR _{max} (<i>t_{HRRmax}</i>) [s]	205	275	730	795	670
Final residue (<i>res</i>) [wt%]	0	3	13	23	32
Time to final residue (<i>t_{res}</i>) [s]	250	310	860	830	850
Average Mass Loss Rate (MLR = 60·(100–res)/ <i>t_{res}</i>) [wt%/min]*	24.0	18.8	6.1	5.6	4.8

*Equal to the average slope of the Residual mass vs. Time curve multiplied by (–1)

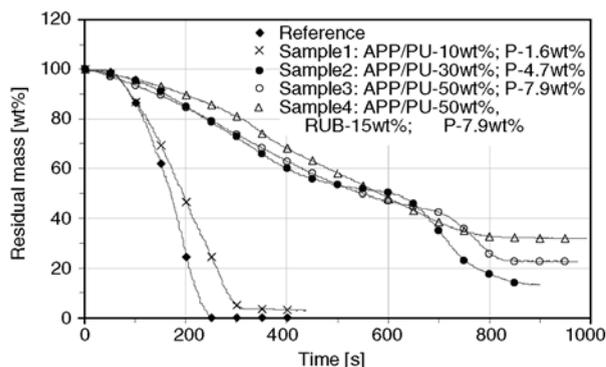


Figure 3. Residual Mass vs. Time in mass loss calorimetric measurement of the compounds

ple 1 was dripping and burnt away completely (see values of *res*). However the HRR_{max} dropped by approx. 50%, the reduction of *MLR* exceeded 20% and $t_{HRR_{max}}$ increased moderately, by 70 s. The flame velocity at horizontal burning reduced moderately, by approx. 6%.

The increase of phosphorus content (Sample 1–3) led to a direct improvement in both UL 94 (up to V-0 grade) and LOI (up to 30). Values of t_{ign} and *res* increased tendentially. At the same time HRR_{max} and *MLR* decreased significantly. Comparing to Sample 1, $t_{HRR_{max}}$ shifted towards the higher ranges, by 455 s (Sample 2) and 520 s (Sample 3). This means an extremely extended term available for escape in case of building or vehicle fire where the interior plastic parts are made of these compounds. Expressive drop of *MLR* values, to approx. a fourth that of Reference could be observed.

The introduction of rubber powder to the compound, containing the APP/PU flame retardant additive system 50.0 wt% on the expense of LDPE/EVA matrix (Sample 4) affected the burning properties quite variously compared to the Sample 3, containing the same amount of APP/PU system. The alteration in the LOI value was negligible. The UL 94 grade kept its value. On the other hand the HRR_{max} decreased by approx. 30%. HRR_{max} being less than a sixth that of the Reference and $t_{HRR_{max}}$ being more than 10 minutes, provides increased chance of escape in case of fire. The amount of *res*

increased by 9 wt%, while a 15% decrease in *MLR* was realized.

3.2. Gas emission

Knowledge about the products of combustion process, mainly about the gases emitted from materials to be applied in the interior of buildings, is important. Even if a material basically is flame-retardant under forced burning conditions it will more or less decompose.

The forced burning can be modelled either by oxygen consumption cone [41] or mass loss calorimeter. The evolved gases can be piped in the measuring cell of an FTIR spectrometer and analysed in line throughout the burning process. The scheme of such a construction is demonstrated in Figure 1. The 3D FTIR spectra of the Reference and Sample 1, 3 and 4 can be seen in Figure 4.

The reference and flame retarded samples differ largely, especially in respect of the maximum absorbance in the wavenumber region characteristic for the CO₂ and CO gas components.

The relative amount of the evolved gases was calculated by integration of the 3D FTIR spectra. The integrals for CO₂ and CO and the CO₂/CO yield ratios are presented in Table 2.

Introduction of 10% APP/PU system reduced the amount of evolved CO₂ and CO by 15 and 19%, respectively (Reference and Sample 1).

The amount of CO₂ and CO decreased with increasing APP/PU content (Sample 1–3). Comparing Sample 1 and 3, a 70 and a 60% decrease in the amount of CO₂ and CO was realized, respectively. Comparing Sample 2 and 3, the drastic cutback in the amount of CO₂ to a value of less than a third resulted in the decrease of CO₂/CO yield ratio to approx. a half.

Sample 4, prepared by incorporation of rubber powder in the composition Sample 3 on expense of LDPE/EVA, gives an increased amount of both CO₂ and CO, compared to the Sample 3. These values, even so, are approx. 50 and 60% those of Reference, respectively.

Table 2. Relative amount of the evolved CO₂ and CO gases. CO₂/CO yield ratios for Reference and Sample 1, 2, 3 and 4

Values evaluated from the FTIR spectra	Reference	1	2	3	4
Relative amount of evolved CO ₂ [-]	12590	10762	9020	2930	6707
Relative amount of evolved CO [-]	83	67	39	26	51
CO ₂ /CO yield ratio [-]	151.7	160.6	231.3	112.7	131.5

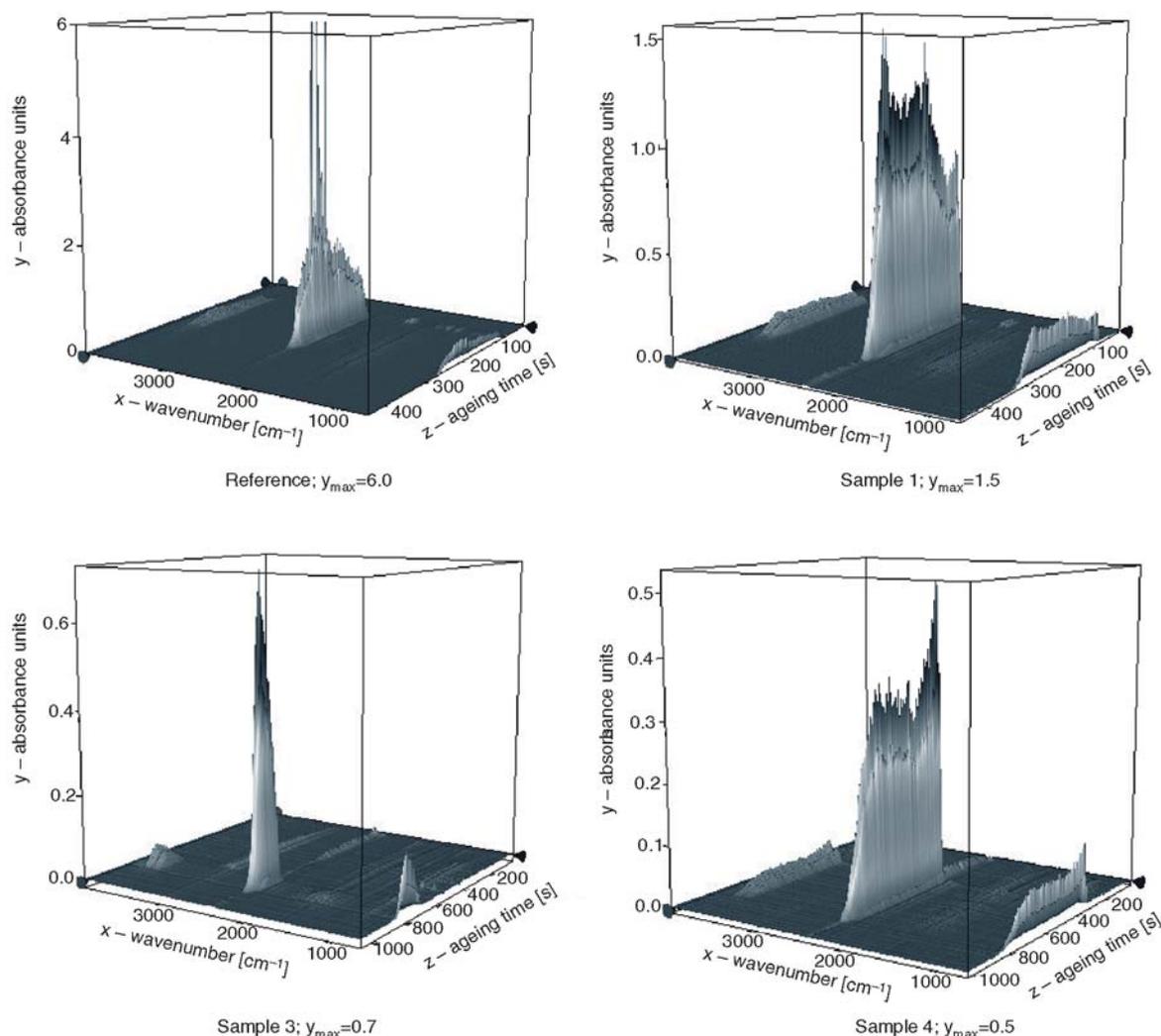


Figure 4. The 3D FTIR spectra of the gases releasing from Reference and Sample 1, 3 and 4, where y = absorbance, x = wavenumber (0–4000 cm^{-1}), z = ageing time (0–350 s)

3.3. Mechanical properties

The values of tensile strength, relative elongation at break, tensile modulus and deviations are shown in Table 3.

Both APP/PU and APP/PU/RUB systems reduce the tensile strength of the compounds, as it was expected, proportional to the amount of the additive. The decrease of relative elongation at break of the compounds with increasing amount of additive is more drastic. It has to be remarked that the introduction of RUB prevents the strong reduction of

elongation at break. The addition of both APP/PU and APP/PU/RUB systems to the LDPE/EVA matrix led to an increase in stiffness. The higher the APP/PU additive content, the higher the tensile modulus (Sample 1–3). Comparing Samples 1 and 3, it increased to a value of more than three times. Preserving the content of the APP/PU system the same (50.0 wt%), addition of rubber powder resulted in a decrease by more than 10% (Sample 3 and 4). The mechanical properties of the compounds suggest, the APP/PU and APP/PU/RUB

Table 3. Values of tensile strength [MPa], relative elongation [%], tensile modulus [MPa] and deviations for Reference and Sample 1, 2, 3 and 4

Tensile properties	Reference	1	2	3	4
Tensile strength [MPa]	11.2 ± 0.6	5.8 ± 0.4	3.7 ± 0.2	2.3 ± 0.1	1.6 ± 0
Relative elongation [%]	1124 ± 23	505 ± 55	185 ± 27	6 ± 0	32 ± 4
Tensile modulus [MPa]	24.7 ± 1.9	27.7 ± 1.9	58.7 ± 0.9	82.3 ± 5.1	70.6 ± 3.4

flame retardant compounds can be used in such applications, where not tensile but compression strength is required from the products prepared from the compounds.

4. Conclusions

Flame retarded LDPE/EVA based polymeric compounds can be formulated by incorporation of an intumescent flame retardant system, consisting of waste polyurethane and ammonium polyphosphate. This system could be applied for utilization of waste rubber as well. The compound containing 40 wt% waste polyurethane and rubber powder as a whole, shows fire retardancy, low HRR_{max} and high of $t_{HRR_{max}}$, which provides chance of escape in case of fire.

The environmental impact of the compounds was detected by IR analysis of the evolved gases during the mass loss calorimetric measurements. The amount of CO₂ and CO decreased with increasing APP/PU content. The rubber powder containing compound had also a considerably reduced CO₂ and CO emission compared to Reference. The APP/PU and APP/PU/RUB systems reduced the tensile strength proportionally to the additive content. The relative elongation at break decreased by the additives more drastically; however, the RUB additive partly inhibited this effect. The introduction of additives led to an increase in modulus.

The processability of compounds containing recycled materials is excellent and applicable as fire retarded thermoplastic rubbery material for engineering purposes such as floor covering or interior panel in construction of buildings.

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