

THERMAL CHARACTERIZATIONS OF THE POLYOLEFIN/NATURAL POLYMERS BLENDS*

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The aim of this work was to obtain of the information referring to the thermal processes of the composite materials having natural polymers. A comparatively study of thermo oxidative behavior of the some polyolefin/wood flour (WF) and lignin (L) blends with variable composition were made. It was remark that materials with a higher percent of the natural polymer present a reduced thermal stability comparatively with the matrix. One can also observed that the introduction as filling materials of the lignin leads to composite materials much stable for thermal point of view than those containing wood sawdust.

Key words: thermal characterization, blends, natural polymers, polyolefin's.

1. INTRODUCTION

The field of natural fiber reinforced thermoplastic composite materials is now rapidly growing both in terms of industrial applications and fundamental research. The use of lignocellulosics as fillers and reinforcements in thermoplastics has been gaining acceptance in commodity plastics applications in the past few years [1].

The lignocellulosics used in thermoplastics can be obtained from several sources, both from forestry and agricultural resources. The physical form can vary from fine powders (wood flour) to fibers (kenaf, flax, sisal and other agro-based materials). The cost and performance of the final composite products dictates the type of lignocellulosic to be used in the plastics. Literature also cites the use of typical plastics such as polyethylene, polypropylene, polyvinyl chloride and also some elastomeric co-polymers for blending with the lignocelluloses [2].

The manufacturing temperature and variety of applications in industry of blends are influenced by the thermal characteristics of the wood flour and

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biodegradable polymer in this study. Therefore, the thermal properties of natural/polyolefin blends were studied by using a thermal analyzer. Thermogravimetric analysis (TG) can measure the moisture content, thermal breakdown and thermal stability of materials [3].

The aim of this study was to investigate the thermal properties of wood-flour and lignin-filled polyolefin blends as a function of the natural content and type.

EXPERIMENTAL

MATERIALS

As a polymer matrix it was used recycled polyethylene (RPE) in the powder shape (0.17 g/min. flow index and 0.94 g/cm³ density) obtained by recycling the packages for bottle drinks. As filling material flax lignin (L) obtained from GRANIT Co Switzerland and wood sawdust (WS) obtained by furniture industries has been used.

In order to achieve a better compatibility between the matrix and the filling material was two consistence agents supplied by EXXON CHEMICAL were used: copolymer ethylene-propylene modified with 0.7% maleic anhydride [Exxelor VA 1803 (C 1803)]; copolymer ethylene-propylene unmodified with 77% ethylene [PE 805 (C 805)].

METHOD

Table 1 shows composition of composite materials obtained by extrusion – press method [5].

Table 1

Experimental program

Sample code	Matrix	Compatibilizing agents		Filling material	
	RPE %	C1803 %	C 805 %	L %	WS %
RPE	100	–	–	–	–
RPE/20%WS	77	3	–	–	20
RPE/25%WS	72	3	–	–	25
RPE/30%WS	67	3	–	–	30
RPE/20%L/C1803	77	–	3	20	–
RPE/30%L/C1803	67	–	3	30	–
RPE/35%L/C1803	62	–	3	35	–

INVESTIGATION METHODS

The TG and DTG curves were registered on a Paulik-Paulik Erdely MOM analyzer with a heating rate of 12°C/min in air atmosphere with a flow of 30 ml/min, in the range of 25–600°C, using a sample mass of 50 mg. For evaluation of the kinetic parameters three calculation methods were applied: Coats-Redfern (CR) [4], Reich-Levi (RL) [5] and Swaminathan-Madhavan (SM) [6].

RESULTS AND DISCUSSION

It was comparatively study the thermo oxidative behavior of the blends with different percent of the natural polymers (wood sawdust and lignin) and recycled polyethylene. Wood sawdust content varied between 20–30%, while the type and percent of the compatibilizing agent (3% C1803) was the same for all samples.

The polyethylene matrix presents a single main decomposition step, in the domain 183–450°C.

From the registered curves patterns (Fig. 1) it can see that wood sawdust/polyethylene blends are thermally decomposed in a specific manner. The three temperature step were identified: the first domain (150–288°C) where probably take place the degradation of some compounds containing wood sawdust, the main stage decomposition (350°C–480°C) both synthetic matrix and filling materials followed final stage has been owing to the products carbonization.

For each sample it was determined the following thermal characteristics: initial decompose temperature (T_i), temperature corresponding to the maximum mass loses (T_m) and final temperature (T_f). From TG/DTG curves the kinetically parameters of the thermo oxidative decomposition reaction: activation energy (E_a), pre-exponential factor, the reaction order (n) and the residue quantity (ΔW) were calculated for each decomposition stage and it is presented in table.

In the first stage, the increase of the WS percent leads to decrease of the T_i and T_m indicating an easily decrease of the thermal stability. This phenomen can be explained by a high of the amorph zone content of wood sawdust and the presence of some compounds which are more susceptible to thermal decomposition.

In the second stage, one can observe to decrease of the initial temperatures with the increase of wood sawdust percent. In comparison with polyethylene for which was registered 79.6 % mass loss, the new created materials became more stable for thermal point of view, mass losses decreasing to 57–49%.

In case of replacement of the wood sawdust with lignin (Fig. 2) can be observed the presence of two decomposition stages. In the first stage, which is

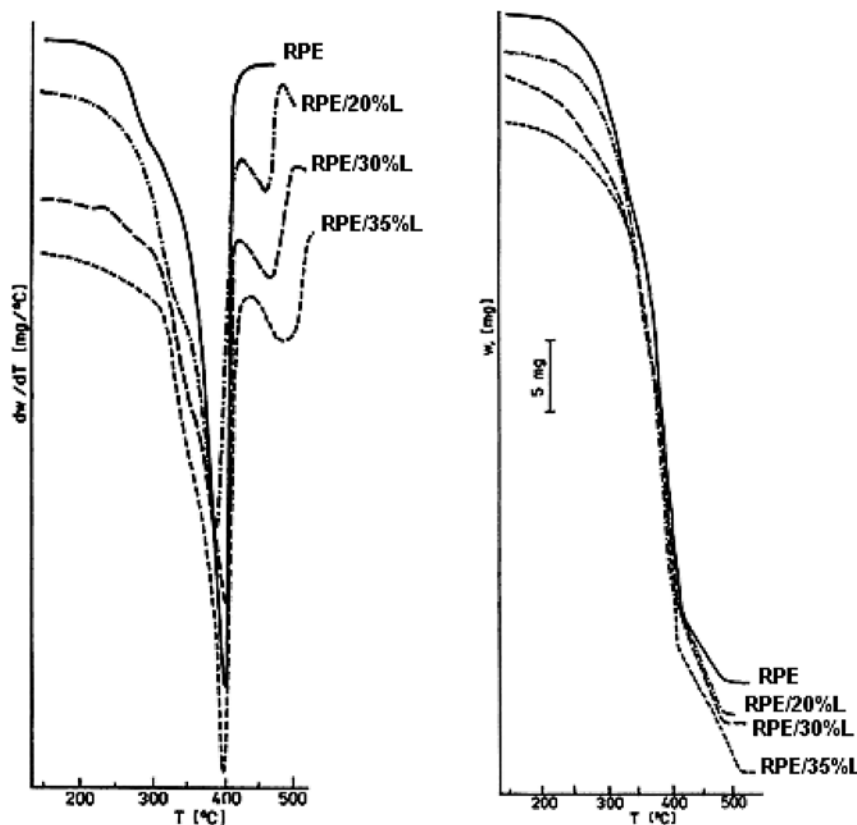


Fig. 2 – TG/DTG curves for blends with different lignin percent.

main decomposition stage, with the increase of the lignin percent T_i shifts to the lower values, while T_m presents an easily increase in comparison with those of the RPE. In this stage has taken place both the decompositions of lignin and recycled polyethylene. Evolution of the E_a presents a growing until a 30% lignin percent being 77.8 kJ/mol after this value she decrease to 44,1 kJ/mol.

The initial temperature values of the blends with lignin decrease from 222°C in case of materials with 20% lignin percent to 176°C for blends with 35% lignin addition. It means that the thermal stability grows with the addition of the lignin.

The loss mass are lower in the second stage of the thermooxidative decomposition processes and initial temperatures increase slowly until 417°C to the 433°C. Like in case of the first stage the activation energy grows until 30% lignin percent and his value is 571.9 kJ/mol, after that she decrease to the 315.4 kJ/mol value at 35% lignin percent. High E_a values show a complex thermal process in this stage. It is known that high temperatures occurred cross linking reactions of the lignin fragments. Low mass losses confirm to form some polymer networks.

Table 4

Thermogravimetric characteristics of the first stage of decomposition process of the blends with variable percent of lignin

Sample	T _i [°C]	T _m [°C]	ΔW [%]	E _{CR} [kJ/mol]	n _{CR}	E _{SM} [kJ/mol]	n _{Sm}	E _{RL} [kJ/mol]
RPE	183	390	79.6	76.18	1.3	46.38	–	–
RPE/20%L/C805	222	388	76.8	77.1	0.6	63.3	0.4	92.8
RPE/30%L/C805	183.5	403	75.6	77.8	0.6	60.8	0.5	80.7
RPE/35%L/C805	176	397	76.8	44.1	0	50.5	0.4	57.7

Table 5

Thermogravimetric data of the second stage of decomposition process of the blends with variable percent of lignin

Sample	T _i [°C]	T _m [°C]	ΔW [%]	E _{CR} [kJ/mol]	n _{CR}	E _{SM} [kJ/mol]	n _{Sm}	E _{RL} [kJ/mol]
RPE/20%L/C805	417	455	14.4	230.8	1.0	164.1	0.8	349.6
RPE/30%L/C805	418.5	461	12.8	571.9	3.8	–	–	497.9
RPE/35%L/C805	433	497	15.2	315.4	1.7	–	–	343.3

CONCLUSIONS

1. For polyethylene/wood sawdust/compatibilizing blends was determined three stage of the thermooxidative decomposition;

2. Introduction of the wood sawdust in the polyethylene matrix decrease the thermal stability of the blends because of the complex structure of the wood sawdust;

3. Changing the wood sawdust with lignin leads to a slower improvement of the thermal stability. For this case the high activation energy E_a values show a complex thermal process in the second stage of the thermal decomposition;

4. At the high temperatures in lignin structures take place complex modification which leads to the formation of the polymer networks.

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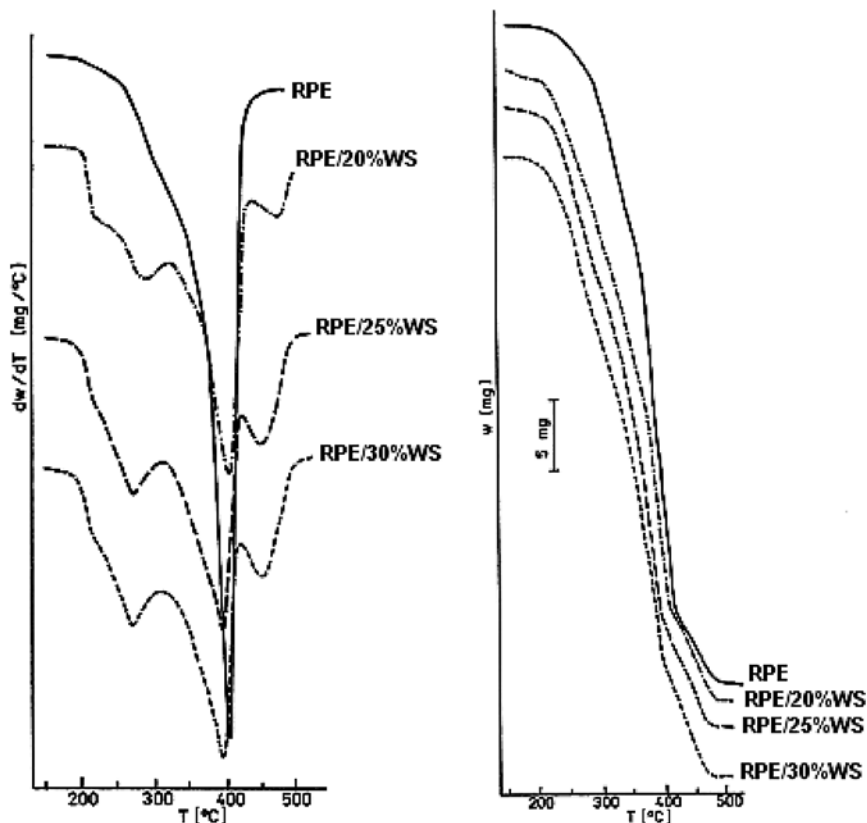


Fig. 1 – TG/DTG curves for blends with different percent of wood sawdust.

Table 2

Thermogravimetric characteristics of the first stage thermooxidative decomposition process of the blends with variable percent of wood sawdust

Sample code	T_i [°C]	T_m [°C]	ΔW (%)	E_{CR} [kJ/mol]	n_{CR}	E_{SM} [kJ/mol]	n_{Sm}	E_{RL} [kJ/mol]
RPE/20%WS	197	288	30	108.7	1.6	–	–	117.6
RPE/25%WS	176	268	26	108.6	1.5	145.1	2.1	129.5
RPE/30%WS	153.5	266	30.8	83.6	0.9	94	1.2	104.9

Table 3

Thermogravimetric characteristics of the second stage thermooxidative decomposition process of the blends with variable percent of wood sawdust

Sample	T_i [°C]	T_m [°C]	ΔW [%]	E_{CR} [kJ/mol]	n_{CR}	E_{SM} [kJ/mol]	n_{Sm}	E_{RL} [kJ/mol]
RPE	183	390	79.6	76.18	1.3	46.38	–	–
RPE/20%WS	323	399	57	147.5	0.9	109.5	0.7	177.05
RPE/25%WS	305	393	52	149.9	1.3	126.8	1.3	172.6
RPE/30%WS	302	396	49.2	124.0	0.9	79	0.7	141.8