

*Dedicated to Professor Ionel Haiduc
on the occasion of his 70th anniversary*

THERMAL INVESTIGATION UPON VARIOUS COMPOSITE MATERIALS

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The influence of content of chemically modified beech wood sawdust, as filler, upon thermal properties of polyethylene (LDPE, HDPE), and polypropylene (PP) - based composites has been studied. A moderate decrease in the thermal properties was evidenced for composites based on polymer matrix / wood sawdust modified with anhydride being related to the increasing content of the filler. For the main temperature domain of the composites decomposition process, the maximum temperature (T_m), respectively the corresponding weight loss values evidence a slightly decrease of the thermal stability for the obtained composite materials. The kinetic parameters E_a (activation energy), $\ln A$ (pre-exponential factor) and n (reaction order) were also determined.

INTRODUCTION

The wood used in wood-plastic composites (WPC's) is most often in particulate form (e.g., wood sawdust) or very short fibers and bundled fibers rather than long individual wood fibers. Products typically contain approximately 50% wood, although some composites contain very little wood and others as much as 70%. The relatively high bulk density and free-flowing nature of wood flour compared with wood fibers or other longer natural fibers, as well as its low cost, familiarity, and availability, is attractive to WPC manufacturers and users. Common species used include pine, maple, and oak. Typical particle are 10 to 80 mesh size.¹ Because of the limited thermal stability of wood, it was believed initially that only thermoplastics that melt or can be processed at temperatures below 200°C could be used in WPC's and currently that is the practice. Most WPC's are made with polyethylene,²⁻⁴ both recycled and virgin, for use in exterior building components. However, WPC's made with wood-polypropylene are typically used in automotive applications and consumer products, and these composites have recently been investigated for use in non-structural building profiles.⁵

Wood-PVC composites typically used in window manufacture are now being sometimes used in

decks and railings as well.⁶ Chemical modification of wood can determine to change its properties and improve its performance. This idea is applied to both solid wood and wood composites.

In order to make property changes, it is necessary to understand the chemistry of the components and the contributions each play in the properties of the resource. Cell wall polymers responsible for the thermal degradation of wood follow the next diagram: hemicelluloses > cellulose >>> lignin.

The thermal behaviors in air of wood-plastic composites have been investigated.

RESULTS

Effect of reaction time on weight percent gain (WPG) for beech wood sawdust

Generally, by increasing the reaction time more than 7 h did not result in significant increases of WPG for beech wood. An increase of WPG for beech wood sawdust (after 7 h treatment with 10 % maleic anhydride - 3.6) is noticed. This may be due to the morphological and structural features, as well as to the degradation reaction of the wood materials.

Characterization of esterified wood filler

The chemical structure of modified wood sawdust (MS) was changed compared to untreated as indicated by FTIR spectra (Fig. 1). The intensity of the 1732 cm^{-1} peak of C=O group due to the

maleation and carboxyl groups of hemicelluloses, and aliphatic ketone or aldehyde in lignin structure increased as a result of the esterification reaction. Also, it was evidenced an increase in the intensity of OH in plane bending vibration at 1382 cm^{-1} for cellulose and hemicelluloses.

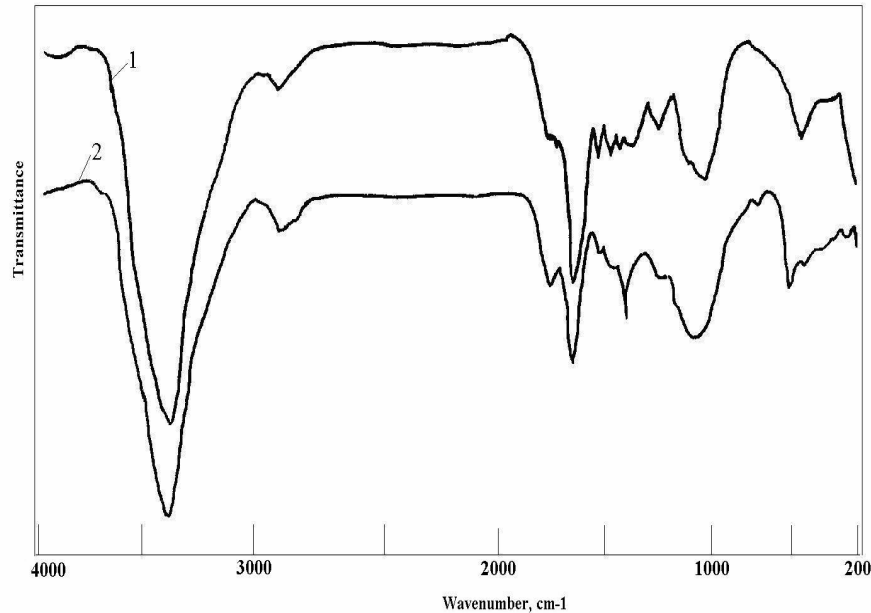


Fig. 1 – FTIR spectra of untreated (1) and esterified (2) wood sawdust samples.

Thermal analysis

The combustion process is significantly influenced by the relative proportion of principle constituents of the wood, namely: cellulose, hemicelluloses, and lignin. The relative proportion of these constituents varies in different wood species. The thermal decomposition behavior of wood-plastic composites primarily depends on its chemical constituents. In addition to the above parameters, experimentally derived kinetic parameters also depend on the specific pyrolysis conditions that include heating rate, compounds ratio, as well as the samples' homogeneity. In Fig. 2-5, the TG/DTG diagrams for all composites are presented. Generally, an increase of wood sawdust ratio in composite materials gives a decrease of weight loss for the main temperature domain (Table 1).

For wood / polymer composites under study, the following thermal characteristics were determined: temperature corresponding to the maximum weight loss (T_m), temperature corresponding to 10 % weight loss (T_{10}), respectively temperature corresponding to

50 % weight loss (T_{50}). The kinetic parameters of the thermo-oxidative decomposition reaction, activation energy (E_a), pre-exponential factor ($\ln A$) and reaction order (n) were calculated, their values being presented in Table 1.

An increase of the wood sawdust ratio gives significant reduction of weight loss corresponding to the maximum temperature (T_{max}) of decomposition process. The temperature domain (T_i-T_f) for the main thermal decomposition process and the corresponding activation energy vary in concordance with the constitutive elements ratio present in composites, as well as the involved polymer matrix (Table 1). The weight loss evidenced at the end of the main decomposition process (W_f) decreases significantly with increasing the modified wood sawdust content in composite materials. The initial and maximum decomposition temperatures, as well as the weight loss within $T_i - T_{max}$ interval are sustained also by the changes of E_a with conversion during degradation (Figures 5-7).

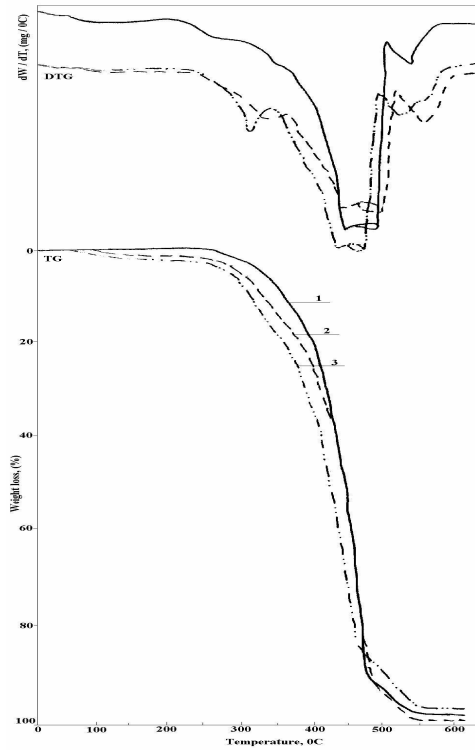


Fig. 2 – DTG and TG diagrams for composites 1 -HDPE/10% MS; 2 -HDPE/25% MS; 3 -HDPE/50% MS.

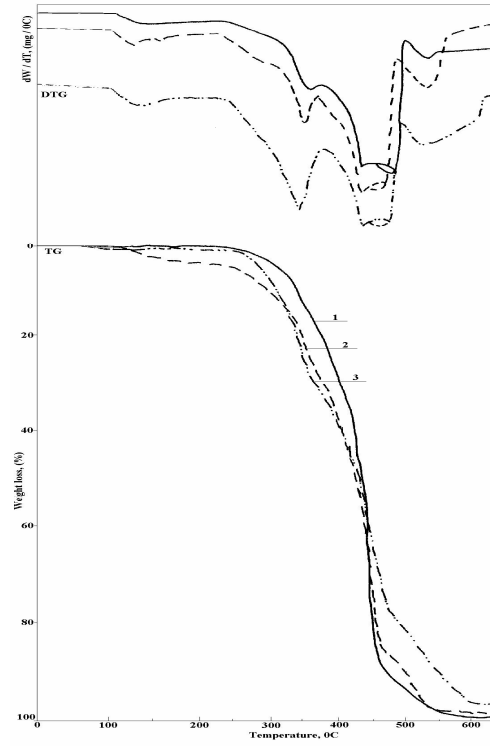


Fig. 3 – DTG and TG diagrams for composites 1 -LDPE/10% MS; 2 -LDPE/25% MS; 3 -LDPE/50% MS.

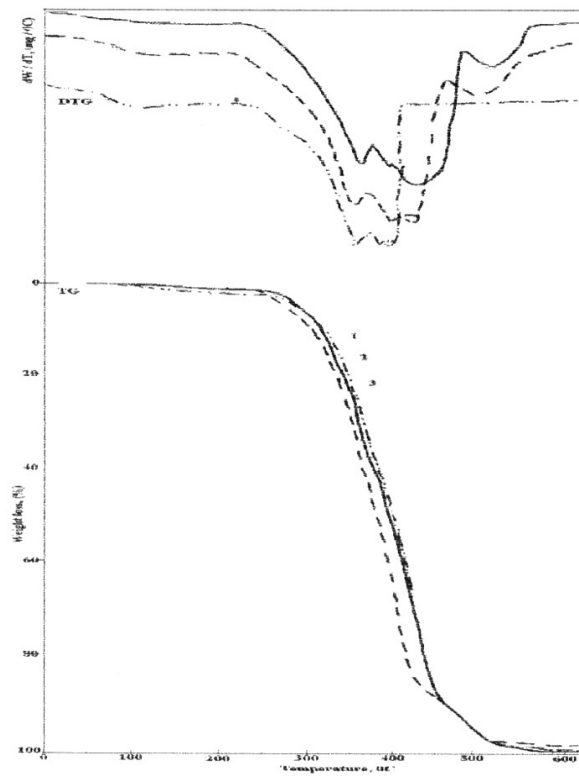


Fig. 4 – DTG and TG diagrams for composites 1 - PP/10% MS; 2 - PP/25% MS; 3 – PP/50% MS.

Table 1

Thermogravimetry parameters for different wood-polymer composite materials

Sample	Temperature domain (T_i-T_f), °C	T_{10} °C	T_{50} °C	T_m °C	W_f %	$\ln A$	Ea, KJ/mol		n	
							ref 10	ref 9	ref 10	ref 9
HDPE/10 %MS	290-500	350	435	480	90.0	11.04	60.92	77.56	0.5	1.00
HDPE/25 %MS	360-510	320	440	470	79.6	6.32	42.74	51.29	0.2	0.71
HDPE/50 %MS	340-475	370	420	440	69.0	10.41	40.39	72.02	0.0	0.40
LDPE/10 %MS	370-487	400	445	459	71.2	17.06	52.14	-	0.0	0.42
LDPE/25 %MS	370-480	390	430	450	56.4	18.25	35.26	-	0.0	0.66
LDPE/50 %MS	380-500	265	320	450	46.4	13.56	66.65	74.47	0.6	0.96
PP/10 %MS	230-470	305	380	420	89.0	10.33	60.36	66.82	0.8	0.86
PP/25 %MS	210-440	290	360	410	86.7	10.41	58.60	64.92	0.7	0.91
PP/50 %MS	240-390	290	345	360	47.5	8.19	46.80	54.00	0.0	0.16

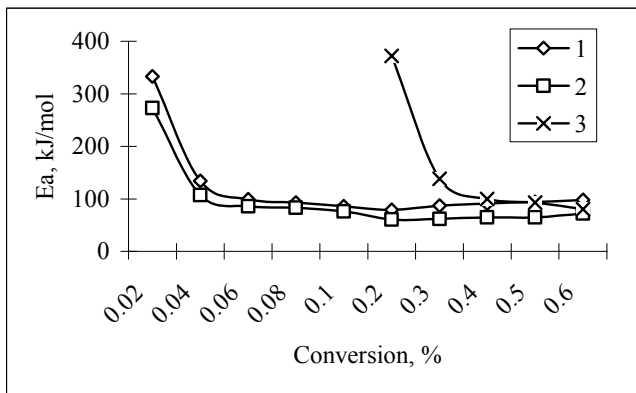


Fig. 5 – Dependence of Ea on conversion for composites degradation process 1 – HDPE/10% MS; 2 – HDPE/25% MS; 3 – HDPE/50% MS.

Fig. 6 – Dependence of Ea on conversion for composites degradation process 1 – LDPE/10% MS; 2 – LDPE/25% MS; 3 – LDPE/50% MS.

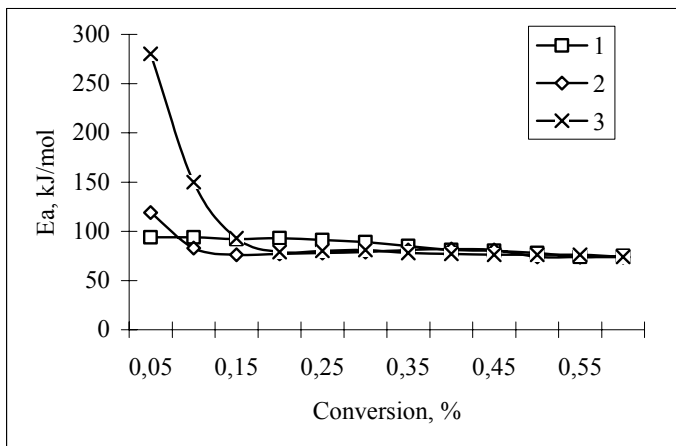
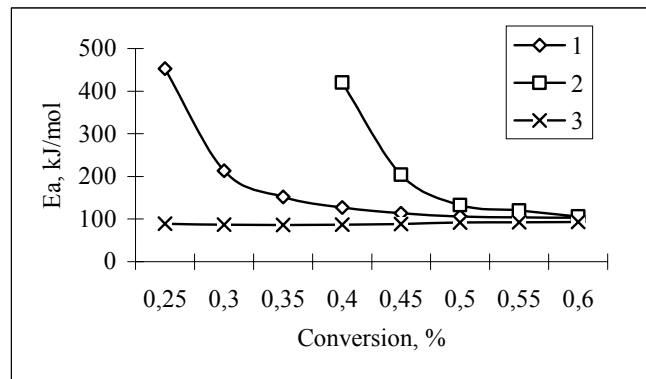


Fig. 7 – Dependence of Ea on conversion for composites degradation process 1 – PP/10% MS; 2 – PP/25% MS; 3 – PP/50% MS.

DISCUSSION

An increase of WPG for modified beech wood sawdust (after 7 h treatment with 10 % maleic anhydride - 3.6) was obtained. FTIR spectra have evidenced the occurrence of the maleation reaction (intensity of the 1732 cm^{-1} peak increases due to esterification).

TG-DTG analysis performed showed differences in thermal behavior of composite materials considered in the study. The thermal diagrams evidence an initial mass loss below $100\text{ }^{\circ}\text{C}$ resulted from the gradually evaporation of absorbed moisture, and another mass loss stage in the temperature domain from $170\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$ occurring through decomposition process of the major constituents present in the wood sawdust (cellulose, hemicelluloses and lignin). Lignocellulosics resources are very susceptible to chemical reactions and thermally decompose between $150\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$: hemicelluloses, mainly between $150\text{ }^{\circ}\text{C}$ and $350\text{ }^{\circ}\text{C}$, cellulose between $275\text{ }^{\circ}\text{C}$ and $350\text{ }^{\circ}\text{C}$, and lignin between $250\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$.⁷ There are also evidenced the main loss stages specific to the polymer matrix.

Generally, the modified wood sawdust/polymer (HDPE, LDPE, PP) composites showed a slightly reduced thermal stability; as the wood sawdust content increased, the thermal stability of the composites slightly decreased. Different weight loss values for the main decomposition process (from TG-DTG analysis) were noticed for all obtained composite materials based on modified wood sawdust, being an evidence of thermal behavior. The weight loss values obtained at the end of decomposition process are significantly lower as the filler content increases in composite materials.

EXPERIMENTAL PART

Wood fillers and esterification agent

Wood sawdust from native sources (beech wood) in concordance with the TAPPI standards was subjected to chemical modification by using maleic anhydride (Aldrich) commercially distributed, as it is presented in the next paragraphs. This native wood species⁸ contains carbohydrates (68-76%), lignin (23-25%) and extraneous materials that can be removed by a solvent (2-11%). In the present work, only

preliminary sieved wood sawdust particles having a particle size $< 0.63\text{ mm}$ were used as filler material.

A. Wood sawdust (preliminary extracted in ethyl-alcohol: benzene mixture) samples were dried at $70\text{ }^{\circ}\text{C}$ in a vacuum oven until constant weight was achieved.

B. Esterification reaction: the filler material (wood sawdust) was dried until constant weight and treated with maleic anhydride (MA) solution in acetone (10% w/w) and heated at reflux temperature ($57\pm 1\text{ }^{\circ}\text{C}$) during 7 h. Moreover, modified wood sawdust (MS) was further extracted in a Soxhlet apparatus for ten hours in acetone in order to eliminate the un-reacted anhydride. Finally, the modified wood sawdust was dried at $105\pm 2\text{ }^{\circ}\text{C}$ in an oven until constant weight was achieved.

FTIR spectroscopy

The KBr (potassium bromide) disk method was used with a Digilab Fourier Transform Infrared (FTIR) spectrophotometer, Model Excalibur FTS-2000. The samples were mixed with KBr to form the pellets that contained 1% powdered sample.

Obtainment of composites

The polymer matrices used in this study were high density polyethylene (HDPE), low density polyethylene (LDPE), and polypropylene (PP) supplied by SNP PETROM, sucursala Arpechim Pitesti, Romania. The composite materials contain 10-50% by weight treated filler (wood sawdust). Mixing of the compounds was performed on a Berstoff-type laboratory roller (Germany), with the cylinders heated at $110\text{--}170\text{ }^{\circ}\text{C}$, the rate of the anterior cylinder being 12 m/min and the friction coefficient 1.2. The compounds were calculated for charges of 0.500 kg. A weighed amount of polymer matrix (HDPE, LDPE, PP) was introduced on the roller, and a continuous sheet was formed on the surface of the anterior cylinder. Then the filling material was gradually added. The total duration of compounding was 10-25 min. Finally, the compounds were laminated as sheets. The sheets thus obtained were transformed through pressing (pre-heating temperature $80\text{--}150\text{ }^{\circ}\text{C}$, pre-heating time 10 min, pressing time 10 min, a pressure of 14 Mpa) into 2 and 4 mm thick plates.

Thermal behavior investigation

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded on a Paulik-Erdey-type derivatograph, MOM Budapest (Hungary), under the following operational conditions: heating rate $12\text{ }^{\circ}\text{C}/\text{min}$, temperature range $20\text{--}600\text{ }^{\circ}\text{C}$, sample weight 50 mg, using powdered samples in platinum crucibles, $30\text{ cm}^3/\text{min}$ air flow, as reference material $\alpha\text{-Al}_2\text{O}_3$. Three or four repeated readings (temperature and weight loss) were performed on the same TG curve, each of them having at least 15 points.

Activation energies of decomposition reactions were determined by using Swaminathan and Madhavan⁹ and Coats-Redfern¹⁰ methods for having a complete image of the thermal behavior of the studied composites (see Table 1). The general equations used were:

$$d\alpha/dt = A \exp(-E_a/RT) [\alpha^m (1-\alpha)^n] [-\ln(1-\alpha)^p] \quad (1)$$

$$\log[1-(1-\alpha)^{1-n}] / [(1-n)T^2] = \log(AR/\beta E_a) - 2.303(E_a/RT) \quad (2)$$

where: α - conversion degree (ratio of the weight loss at time "t" and at the end of the process), t - time of reaction, A - pre-exponential factor, E_a - activation energy of decomposition,

R - universal gas constant, T- temperature, n- reaction order, m, p - exponents of the conversion function, β - heating rate.

The changes of Ea with conversion during degradation were evaluated by using Reich-Levi methods^{11,12} (see Figures 5-7).

CONCLUSIONS

Wood-plastic composites are hybrid materials that combine wood sawdust and synthetic thermoplastics.

Thermal properties of composite materials considered in the study were influenced by the nature and components ratio, and distribution of the solid component in composite material.

For the temperature domain in which processing of the studied composites is to be performed, the used filler material slightly reduces the apparent thermal stability of the polymer matrix due to its complex structure, some specific biopolymer wood constituents being very susceptible to the thermal decomposition.

As a general behavior, with increasing the modified wood sawdust content in composite materials, the weight loss evidenced at the end of the thermal decomposition process exhibits lower values. The increase of the modified wood sawdust content leads to a lower maximum temperature value indicating a slightly decrease of the thermal stability.

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