# Effect of Chemical Modification with Maleic, Propionic, and Succinic Anhydrides on Some Properties of Wood Flour Filled HDPE Composites

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One of the biggest disadvantages of wood, as a potential reinforcement for thermoplastics, is its hydrophilicity. The aim of this study was to evaluate the effect of chemical modification of wood flour on mechanical, thermal, and fire properties of filled high-density polyethylene composites. For this purpose, aspen flour was modified with maleic, propionic, and succinic anhydrides. The modified wood flour and high-density polyethylene were compounded into pellets by single-screw extrusion, and test samples were prepared by injection molding. Tensile and flexural tests, impact testing, limiting oxygen index, TGA, and SEM analyses were conducted both for modified and un-modified samples. Based on the test results, chemical modification enhanced the properties of thermoplastic composites. Depending on the chemical concentrations, the flexural, tensile, and impact strengths of the modified flour filled HDPE composites were improved slightly, while the tensile and flexural moduli of the samples were increased significantly. The limiting oxygen index (LOI) levels of samples with modified wood flour were slightly improved, and succinic anhydride provided higher LOI levels compared to the samples with other anhydrides. This showed that the composites filled with chemically modified wood flour were slightly more thermally stable than control samples. It appears that wood flour modified with maleic, propionic, and succinic anhydrides can be successfully utilized as filler in polymer matrices.

*Keywords: Modified wood flour; Anhydrides; Composite; Mechanical properties; Thermal properties*

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## INTRODUCTION

The production and application of bio-based materials such as wood-plastic composites (WPCs) and natural fiber plastic composites (NFPCs) has been getting more popular (Bismarck *et al.* 2005; Bogoeva-Gaceva *et al.* 2007; Thomas *et al.* 2011; Kiziltas *et al.* 2014). In 2012, wood-plastic composites and natural fiber plastic composites constituted about 15% of European total composite production, with a volume of 352,000 tonnes (Carus *et al.* 2012). Wood-plastic composites are widely used in outdoor applications for floors, railings, fences, landscaping timbers, cladding and park benches, molding and trim, and window and door frames (Clemons 2002; Kylosov 2007).

Wood-plastic composites have some superior properties compared to both wood fiber and plastics, but they still need some improvements to meet consumer expectations (Ibach and Clemons 2006). It was reported that when wood fiber loading increased in the polymer matrix, dimensional stability and resistance against biological attacks (fungus and insects) of WPCs were decreased and discoloration by UV in WPCs were increased (Clemens *et al.* 2004; Donmez Cavdar *et al.* 2011). Additionally, the level of adhesion between the wood fibers and the polymer matrix has a significant effect on the properties of WPCs. The mechanical properties are especially affected because of the interaction at the interface of the two incompatible components, wood (polar nature of fiber due to hydroxyl groups) and plastic (non-polar matrix). Therefore, it is necessary to improve the interfaces between the wood and the polymer matrix. This can be accomplished by modifying the hydrophobic phase or hydrophilic phase into a joint interphase. Examples of this method include modification of the wood fibers by chemical reaction with a coupling agent or coating the wood fibers with resins/chemicals (Raj and Kokta 1991; Sundar *et al.* 2004; Rowell 2005; Sundar 2005; Ibach and Clemons 2006).

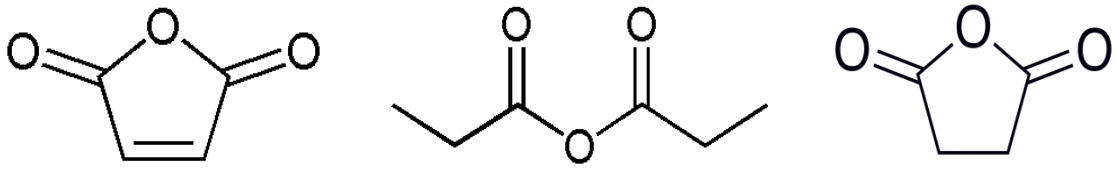
Chemical modification of the wood cell wall employs the reaction of a reagent with the polymeric compound of wood and the subsequent formation of a covalent bond between the reagent and the wood substrate (Hill 2006). When wood is modified with acetic anhydride or other anhydrides, the anhydrides are partly converted to acetic acid or other acids as by-products. The esterification of wood by a linear chain anhydride results in hydroxyl groups in the wood cell walls being replaced with the acyl adducts that are less polar (Rowell 2005; Hill, 2006; Farahani and Taghizadeh 2010). This technique can enhance the adhesion at interfaces between wood fibers and the polymer matrix, improve dimensional stability, decrease moisture content, and increase the durability of wood composites (Raj and Kokta 1991; Dinwoodie 2000; Sundar *et al.* 2004; Lyon *et al.* 2008). Larsson-Brelid *et al.* (2006) studied the properties of WPCs made with solid wood modified by acetic anhydride. They reported that the WPCs could be successfully produced on a semi-industrial scale and made some improvements to the process such as lowering water uptake during water soaking and reducing moisture sorption at 80% relative humidity (RH) and 20 ºC. The effects of anhydride (especially acetic anhydride) chemically modified wood/wood fiber on the biological and moisture properties of WPCs have been investigated in several studies, but there have been few studies on the effects of anhydride modification of wood on the mechanical and thermal properties of WPCs. Studies that have addressed the effect on mechanical properties show conflicting results. Some reported that acetylation improved the mechanical properties of WPCs (Tserki *et al.* 2006; Lisperguer *et al.* 2007; Ozmen *et al.* 2013), while others reported that acetylation adversely affected the mechanical properties of the composites (Luz *et al*. 2008; Mat Taib *et al.* 2010). Today, most studies are focused on the acetylation process with acetic anhydride, while limited studies are available on the use of other anhydrides in WPCs such as maleic, succinic, and propionic anhydrides. However, MA has been used in WPCs as a coupling agent to improve compatibility between wood and polymer matrix by grafting with PE/PP polymer matrix (Maldas and Kokta, 1991). Cantero *et al.* (2003) investigated effect of fiber treatment with maleic anhydride (MA) and maleic anhydride grafted polypropylene (MAPP) on wettability and mechanical properties of flax/propylene composites. They concluded that the treatment of flax fiber improved the wettability and mechanical properties of the composites in comparison to samples with untreated fibers.

The objective of this study was to investigate the effect of chemical modification of wood flour with various anhydrides on the mechanical and thermal properties of high density polyethylene composites filled with wood flour. Chemical modification of aspen wood flour was carried out with maleic, propionic, and succinic anhydride at varying concentrations. Tests were performed on the HDPE composites filled with modified wood flour and control samples of HDPE composites filled with unmodified wood flour, and the results were analyzed and compared.

## EXPERIMENTAL

### Materials

In this study, aspen (*Populus euramericana*) wood flour was obtained from plane machinery off-cuts and was used as a lignocellulosic material. Aspen, which is a fast growing hardwood with wide cells and easy to penetrate (Rowell 1984), has been extensively used due to low cost and lightweight in wood based industry. The off-cuts were granulated into 45-mesh size fibers using a Wiley mill. High-density polyethylene (HDPE) with a density of 0.96 g/cm$^3$ and a melt flow index rate (190 °C, 2.16 kg) of 5.5 g/10 min was supplied by Petkim Petrochemical Company in Izmir, Turkey. Maleic anhydride (MA) with a density of 1.48 g/cm$^3$ (20 °C) and a melting point of 52.8 °C, propionic anhydride (PA) with a density of 1.01 g/cm$^3$ (20 °C) and a melting point of -45 °C, and succinic anhydride (SA) with a density of 1.503 g/cm$^3$ (20 °C) and a melting point of 120 °C were purchased from Merck (Germany). The chemical structures of the anhydrides are shown in Figure 1 (Rowell 2005). Xylene and acetone were also obtained from Merck.



a) maleic anhydride b) propionic anhydride c) succinic anhydride

**Fig. 1.** The chemical structures of maleic anhydride (a), propionic anhydride (b) and succinic anhydride (c)

### Methods

*Chemical modification of wood flour with the anhydrides*

The chemical modification procedure of wood flour with anhydrides at various concentrations is shown in Table 1.

Before the modification, maleic and succinic anhydrides were dissolved in xylene (1:5) and acetone (1:4), respectively. The anhydrides were dissolved in the least possible amount of solvent. However, propionic anhydride was used without solvent or catalyst since it was already in liquid form. The aspen wood flour (WF) was oven dried and weighed. Afterwards, the WF was placed in a glass reactor and treated with the anhydrides for about 10 min by stirring.

**Table 1.** Procedure of Chemical Modification of Wood Flour

| Reagent | Ratio of reagent (wt.% of wood flour) | Ratio of anhydride/solvent and solvent type | Temperature and time | Treatment code | Weight percent gain (%) |
|---|---|---|---|---|---|
| Maleic Anhydride | 5 | 1/5 - Xylene | 130 °C and 3 h | M5 | 4.6 |
| | 10 | | | M10 | 9.4 |
| | 15 | | | M15 | 12.6 |
| Propionic Anhydride | 5 | Neat (no solvent) | 120 °C and 3 h | P5 | 2.5 |
| | 10 | | | P10 | 4.0 |
| | 15 | | | P15 | 5.7 |
| Succinic Anhydride | 5 | 1/4 - Acetone | 130 °C and 3 h | S5 | 4.7 |
| | 10 | | | S10 | 9.4 |
| | 15 | | | S15 | 14.7 |

Maleic and succinic anhydride treated WF was prepared by reaction at 130 °C for 3 h in a drying-oven based on the studies of Serin (2005) and Dizman (2005), respectively. In the case of propionic anhydride, a treatment temperature of 120 °C was used, following a study performed on particleboard by Papadopoulos and Gkaraveli (2003). At the end of the reaction, the WF was washed with acetone and deionized water to remove the unreacted chemicals, by-products, or solvents. Afterwards, they were dried at 103 ± 2 °C to a constant oven-dry weight and weighed to determine weight percentage gain (WPG). The weight percentage gain of the chemical modification of wood flour with the anhydrides is shown in Table 1.

*Preparation of injection molded WPCs*

The oven-dried modified wood flour, HDPE and wax (WF/HDPE/wax ratio of 25/72/3 by weight) were mixed and processed in a single-screw extruder with L/D 30 (Teknomatik Co., Turkey) at 40 rpm screw speed. The raw materials were fed into the main feed throat. The barrel temperatures of the extruder were controlled between 170 and 190 °C for five zones. The extruded strand passed through a water bath and was subsequently pelletized. These pellets were granulated and then dried before the injection molding. The temperature used in the HDX-88 injection molding machine (Ningbo Haida Plastic Machinery Co., Ltd., China) was 180 to 200 °C from feed to die zone. The pellets were injected at an injection pressure of 102 kg/cm$^2$ with an injection speed of 80 mm/s to produce the test samples.

The sample codes of WPCs were assigned as the same codes as for the chemical modification of the wood flour (Table 1). Also, unmodified wood flour filled HDPE composites (control) having the same formulation with modified composites were manufactured as a reference.

*Mechanical properties*

Tensile and flexural tests were conducted according to ASTM D638 (2007) and ASTM D790 (2007), respectively, at room temperature with a universal mechanical testing machine (Zwick/Roell, model Z010; Germany) with a load capacity of 10 kN. Impact testing was performed according to ASTM D256 (2007) at room temperature with a pendulum impact tester (Zwick, HIT5.5P; Germany). The notches were made using a

notching cutter (Ray-Ran Test Equipment, Ltd., Polytest; UK). Ten samples for each group were tested for tensile, flexural, and impact properties.

*Fire performance with limiting oxygen index (LOI)*

The LOI measurements were carried out according to ASTM D 2863 (2000) using a limiting oxygen index chamber (Dynisco, Germany). In the LOI test, all samples were placed in a vertical glass column using a sample holder, and the gas flow (oxygen and nitrogen) was adjusted in accordance with the standard. Each sample was ignited with a flame and burned downward into the unheated material. Then, the minimum oxygen concentrations required to support combustion were recorded as a percentage for all samples. Five samples for each group were used for the LOI measurements.

*Thermogravimetric analysis (TGA)*

Thermogravimetric analysis (TGA) of the samples was performed with a Shimadzu TGA-50 thermal analyzer (Japan) at a heating rate of 10 °C/min under nitrogen with a 20 mL/min flow rate. The samples were heated from room temperature to 700 °C. During the heating and pyrolysis, the change in weight loss was monitored continuously for each 5 mg sample.

*Scanning electron microscopy (SEM)*

Morphologic properties of the samples were analyzed with a JEOL JSM-5500 scanning electron microscope (Japan) operating at an accelerating voltage of 10 kV. The fracture surface of each sample was prepared by sputtering with gold.

*Statistical analysis*

The results were analyzed with SPSS 13.0 (SPSS, USA) statistical package software. In this study, Duncan's mean separation test and analysis of variance test (ANOVA) were chosen (alpha = 0.05) to determine homogeneity in the groups of composites and the effect of anhydride concentrations on the mechanical properties of modified wood flour filled HDPE composites.

## RESULTS AND DISCUSSION

### Mechanical Properties

*Modification with maleic anhydride*

The mechanical properties of HDPE composites filled with maleic anhydride modified wood flour and Duncan's mean separation test results are shown in Table 2. The test results showed that the concentration ratio of MA affected the mechanical properties of the samples.

Tensile strength (TS) values depending on concentration ranged from 18.80 MPa to 20.98 MPa. The highest value was obtained from the samples produced by modifying WF at 5% MA concentration. Although enormous changes were not observed between the controls and modified samples, some statistical differences were detected, as could be seen from the homogeneity groups. Tensile modulus (TM) of the samples increased with the rising concentration of MA due to increasing stiffness of the composites. Compared to

control group, composites produced with 15% MA modified wood flour provided 23% higher TM values.

**Table 2.** Mechanical Properties of HDPE Composites Filled with Modified MA Wood Flour

| ID | TS (MPa) | TM (MPa) | EB (%) | FS (MPa) | FM (MPa) | IS (kJ/m$^2$) |
|---|---|---|---|---|---|---|
| Control | 20.02$^{b}$(0.05) | 575.61$^{c}$(7.71) | 7.80$^{a}$(0.59) | 32.54$^{d}$(0.30) | 1522.69$^{c}$(38.27) | 3.81$^{a}$(0.20) |
| M5 | 20.98$^{a}$(0.13) | 637.41$^{b}$(16.35) | 6.69$^{b}$(0.50) | 34.18$^{c}$(0.40) | 1708.20$^{b}$(46.99) | 3.63$^{a}$(0.28) |
| M10 | 18.80$^{d}$(0.16) | 639.17$^{b}$(11.20) | 6.82$^{b}$(0.34) | 35.41$^{b}$(0.48) | 1841.94$^{a}$(76.76) | 3.35$^{b}$(0.24) |
| M15 | 19.48$^{c}$(0.05) | 710.79$^{a}$(8.08) | 6.95$^{b}$(0.13) | 35.99$^{a}$(0.22) | 1820.37$^{a}$(39.23) | 3.37$^{b}$(0.28) |

TS: Tensile Strength; TM: Tensile Modulus; EB: Elongation at Break; FS: Flexural Properties; FM: Flexural Modulus; IS: Impact Strength
Groups with same letters in each column indicate no statistical difference ($p<0.001$) between the samples according to Duncan's multiple range test
The values in the parentheses are standard deviations

Regardless of MA concentration, MA modified samples had lower elongation at break (EB) values compared to control samples. In the case of impact strength (IS), it was slightly decreased with the increase of MA concentrations. The effects of chemical modification on TM and IS of the composite samples can be explained based on the principle that the wood flour was rendered more rigid by the modification.

Flexural strength (FS) values of the samples increased with the increase in concentration. FS values were found to be between 32.54 and 35.99 MPa, depending on concentration. The greatest increase in FS was found in samples modified with 15% concentration. Flexural modulus (FM) also increased by using MA modified WF. Although the greatest increase rate was obtained by using 10% MA concentration, there were no significant differences in FM values between 10 and 15% MA concentration.

Based on these findings, mechanical properties of thermoplastic composites filled with MA modified wood flour were generally higher than those of unmodified wood flour filled thermoplastic composites. This improvement can be explained on the basis of increased compatibility of wood flour and polymer matrix due to a reduction of polarity between them (Sundar 2005; Ozmen *et al.* 2013a,b; Tserki *et al.* 2013). On the other hand, when MA concentration increased, a small reduction in tensile strength was observed. Burgstaller and Stadlbauer (2012) observed a small reduction on TS of chemically modified wood plastic composites with anhydrides. They noted also this small reduction could be due to less interaction between WF and polymer, therefore less maximum stress could be applied to the composites and this could be compensated via minor modification of production parameters. Similar explanations were given to indicate inferior interaction between acetylated wood fiber and HDPE (Mat Taib *et al.* 2010) and modified cellulose fiber with alkenyl succinic anhydride and PP (Felix and Gatenholm 1993). Mat Taib *et al.* (2010) also reported that the poor fiber-matrix interaction might hinder effective transmission of stress from matrix to fiber and cause a reduction in composite properties at high levels of acetylation.

*Modification with propionic anhydride*

The mechanical properties of HDPE composites filled with propionic anhydride modified wood flour and Duncan's mean separation test are shown in Table 3. The ANOVA showed that the concentration ratio of PA affected the mechanical properties of the samples.

**Table 3.** Mechanical Properties of HDPE Composites filled with Modified PA Wood Flour

| ID | TS (MPa) | TM (MPa) | EB (%) | FS (MPa) | FM (MPa) | IS (kJ/m$^2$) |
|---|---|---|---|---|---|---|
| Control | 20.02$^{b}$(0.05) | 575.61$^{d}$(7.71) | 7.80$^{a}$(0.59) | 32.54$^{c}$(0.30) | 1522.69$^{c}$(38.27) | 3.81$^{b}$(0.20) |
| P5 | 21.04$^{a}$(0.11) | 598.69$^{c}$(1.03) | 7.56$^{a}$(0.40) | 34.12$^{b}$(0.09) | 1672.34$^{b}$(9.25) | 3.76$^{b}$(0.18) |
| P10 | 20.17$^{b}$(0.17) | 670.23$^{a}$(6.92) | 6.19$^{b}$(0.08) | 36.79$^{a}$(0.64) | 1866.19$^{a}$(69.77) | 4.14$^{a}$(0.09) |
| P15 | 21.15$^{a}$(0.28) | 609.53$^{b}$(6.52) | 7.73$^{a}$(0.22) | 34.12$^{b}$(0.40) | 1654.74$^{b}$(10.51) | 4.16$^{a}$(0.12) |

TS: Tensile Strength; TM: Tensile Modulus; EB: Elongation at Break; FS: Flexural Properties; FM: Flexural Modulus; IS: Impact Strength

Groups with same letters in each column indicate no statistical difference ($p<0.001$) between the samples according to Duncan's multiple range test

The values in the parentheses are standard deviations

The TS values ranged from 20.02 to 21.15 MPa, depending on the concentration of PA. The TS values of the samples increased slightly with the increase of PA concentration. The highest TS values were obtained at 5 and 15% concentrations of PA in comparison with the other groups. PA modification of WF increased TM values at all concentrations. The TM of the samples was increased until 10% PA concentration, and then a small decrease was observed, unlike the TM of MA and SA. EB was slightly decreased in the samples that were produced by PA modified wood flour in comparison with the control samples. However, the decrease in EB was not statistically different ($p<0.001$) from the control samples, except for 10% PA treated samples. Furthermore, the decrease in EB depending on concentration level of PA was observed to be inversely proportional to the TM values.

The FS values depending on concentration were found to be between 32.54 MPa and 36.79 MPa. The flexural strength and modulus of the samples were increased with PA modification for all concentration levels. Both properties were increased until 10% PA concentration, and then a small decrease was observed, unlike the FS and FM of MA and SA. Modifying wood flour with PA gave a 23% improvement in the flexural modulus of the samples compared to control samples. In the case of IS values of the samples, there was an increasing trend until 10% PA concentration.

The lowest WPG values were obtained for PA because it was not used with a solvent or catalyst during the modification of wood flour. However, this was not reflected in the mechanical properties of the composites. The tensile and flexural moduli of samples with PA were significantly ($p<0.001$) increased, although they had lower WPG than other anhydrides. Li *et al.* (2000a) stated that the reaction rate was decreased with the use of solvent due to dilution of chemicals. Due to a similar reason as for MA samples, use of high level of PA reduced the mechanical properties, and the best results for PA were detected at 10% concentration (Table 4). In addition, a linear increase was not seen in the mechanical properties when the concentration of anhydrides increased. Another reason for this reduction and fluctuation may be due to insufficient washing to remove unreactive

chemicals, byproducts, or solvents after modification that may occur with an increase in the WPG of PA or the other anhydrides. Ozmen *et al.* (2013b) claimed that application of the Soxhlet cleaning procedure after acetylation had more of a positive effect on the mechanical properties of WPC rather than simply washing with water. It is known that the success of chemical modification of wood (fiber) for WPC depends on several factors: the types of the chemical, solvent, or catalyst, the degree of substitution, the method used, the reaction time and temperature, chemical composition of the fiber, and removal of unreacted chemicals after modification (Rowell *et al.* 1994; Mahlberg *et al.* 2001; Hill 2006; Ozmen *et al.* 2013b).

*Modification with succinic anhydride*

The mechanical properties of HDPE composites filled with succinic anhydride modified wood flour and Duncan's mean separation test are shown in Table 4. The concentration ratio of SA affected the mechanical properties of the samples.

**Table 4.** Mechanical Properties of HDPE Composites filled with Modified SA Wood Flour

| ID | TS (MPa) | TM (MPa) | EB (%) | FS(MPa) | FM (MPa) | IS (kJ/m$^2$) |
|---|---|---|---|---|---|---|
| Control | 20.02$^{b}$(0.05) | 575.61$^{d}$(7.71) | 7.80$^{b}$(0.59) | 32.54$^{c}$(0.30) | 1522.69$^{c}$(38.27) | 3.81$^{a}$(0.20) |
| S5 | 20.48$^{a}$(0.27) | 595.95$^{c}$(16.04) | 10.03$^{a}$(2.05) | 31.97$^{d}$(0.31) | 1343.96$^{d}$(20.22) | 3.74$^{a}$(0.19) |
| S10 | 19.94$^{b}$(0.21) | 614.82$^{b}$(7.90) | 6.99$^{b}$(0.33) | 35.07$^{b}$(0.72) | 1720.79$^{b}$(65.49) | 3.63$^{a}$(0.14) |
| S15 | 19.70$^{c}$(0.20) | 648.80$^{a}$(7.08) | 6.96$^{b}$(0.46) | 36.29$^{a}$(0.48) | 1785.45$^{a}$(25.52) | 3.40$^{b}$(0.18) |

TS: Tensile Strength; TM: Tensile Modulus; EB: Elongation at Break; FS: Flexural Properties; FM: Flexural Modulus; IS: Impact Strength

Groups with same letters in each column indicate no statistical difference ($p<0.001$) between the samples according to Duncan's multiple range test.

The values in the parentheses are standard deviations.

The TS values depending on concentration ranged from 19.70 MPa to 20.48 MPa. The highest values were obtained from the samples produced by modifying wood flour at 5% SA concentration. Similar to MA modification, a meaningful change was not observed for the TS values over 5% SA concentration. As with MA, TM of the samples was increased with the increase in SA concentration. A 13% improvement in TM was observed at 15% concentration in comparison to that of control samples. The highest EB values of the samples were obtained from those modified with 5% concentration of SA similar to TS values of the samples. The FS values depending on concentration were found to be between 32.54 and 36.29 MPa. An increase in the SA concentration levels caused an increase in FS values, which is similar to the case with MA samples. The FM values were also enhanced with the use of SA in the modification of wood flour. The IS of the samples were slightly decreased with the increase of SA concentration, similar with MA modification.

The SA modification of aspen wood flour positively affected the mechanical properties of the composite and had a similar trend to MA modified flour. It appears that substitution of hydrophilic hydroxyl groups of wood flour with succinyl groups renders the wood flour surface more hydrophobic and therefore increases compatibility with the polymer matrix. Additionally, the upward trend in tensile and flexural moduli as concentration (WPG) increased may be due to the fact that moisture sorption would decrease and cause more brittle samples. Rowell *et al.* (1994) studied the modification of

lignocellulosic materials with succinic anhydride at several WPGs and temperatures to form cellulose reinforced thermoplastic composites. They reported that using high reaction temperatures affected the crosslinking of lignin in wood flour.

## Limiting Oxygen Index

Figure 2 shows LOI levels of HDPE composites filled with modified wood flour. The LOI levels of all composites were in the range from 22.5 to 24.5. The LOI levels of SA modified samples increased with concentration. Succinic anhydride provided higher LOI levels compared to the samples with other anhydrides, and the LOI level of the samples with anhydrides was slightly higher than that of control samples. PA and MA didn't have a significant effect on the flammability of the composites. Li *et al*. (2000b, 2001) reported that the LOI levels of wood modified with acetic and propionic anhydrides were found to be the same as those of unmodified wood samples. This means that the rate of oxygen consumption was approximately the same for control and modified wood flour filled composite samples (Rowell 2005).

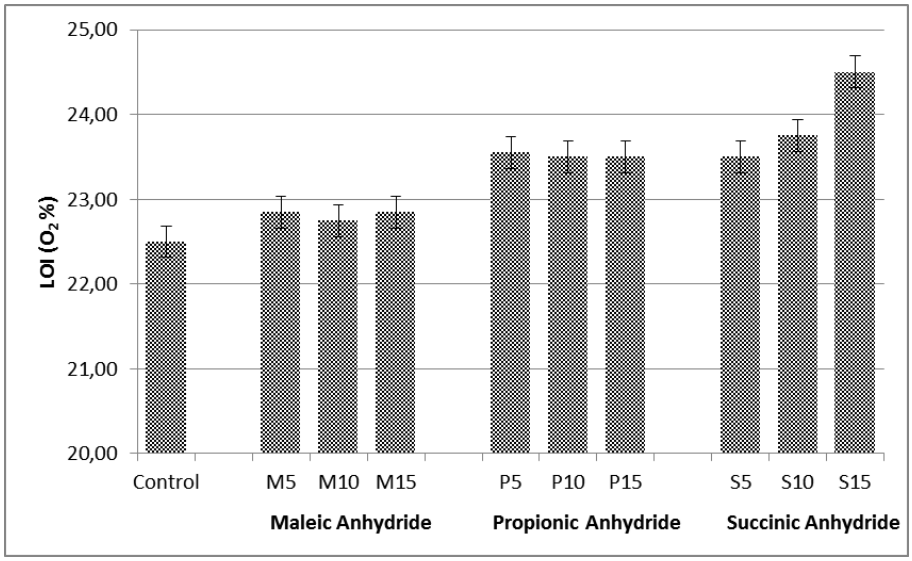



**Fig. 2.** LOI levels of HDPE composites filled with modified wood flour

According to ISO 4589 (1996) the samples with modified succinic anhydride at 15% concentration were in the "limited fire retardant or limited fire resistance material (LOI level 24-28)" group, while the other composite samples were in the "flammable or combustible material (LOI level ≤ 23)" group.

## Thermogravimetric Analysis

Lignocellulosic materials were exposed to intense heat during composite fabrication. Therefore, a thermal analysis was necessary to determine the influence of the fiber/flour addition into the polymer matrix on the thermal stability of the composites and to confirm any degradation processes occurring during the manufacturing of composites (Arbelaiz *et al.* 2006). The thermogram (TG) curves determine the thermal degradation and stability of the materials and weight loss during thermal degradation. The TG curves of

HDPE composites filled with modified wood flour at 5% and 10% concentrations are given in Fig. 3.

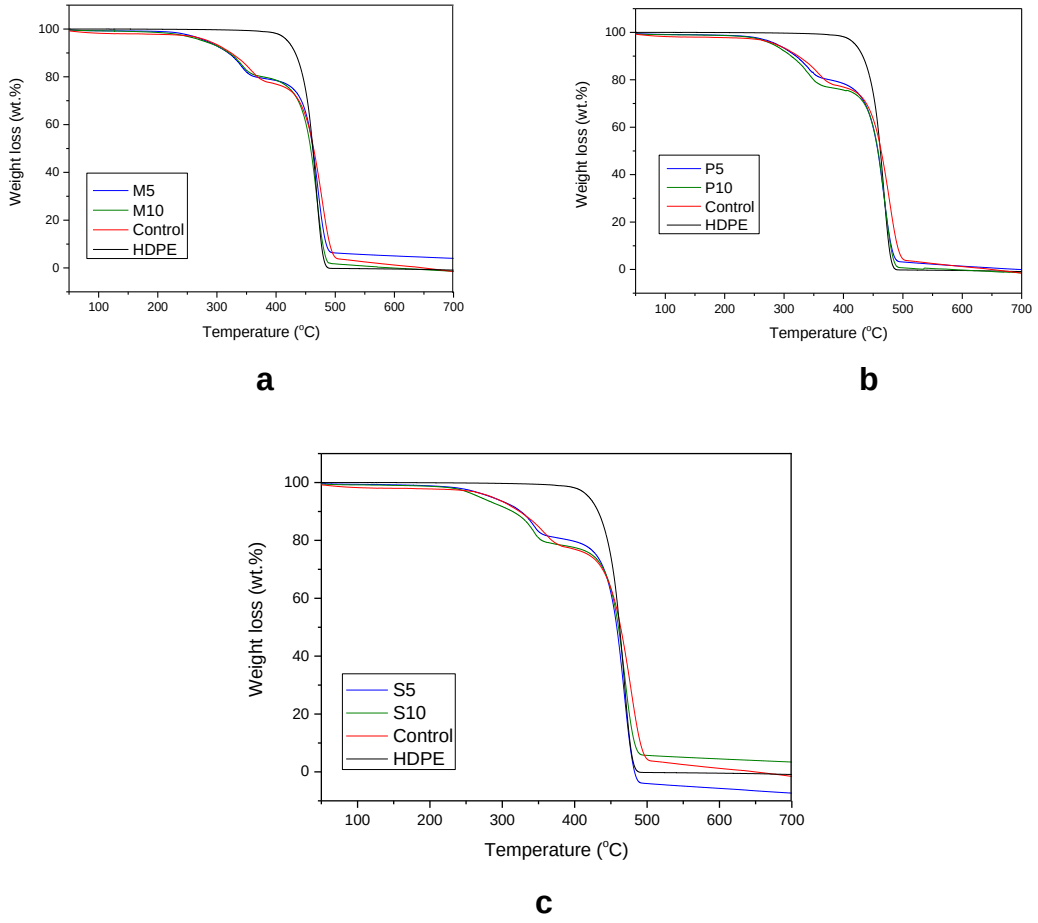



**Fig. 3.** TG and DTG curves of HDPE composites filled with modified wood flour at 5% and 10% concentration: (a) maleic anhydride, (b) propionic anhydride, and (c) succinic anhydride

Neat HDPE showed a one-step decomposition process, while two stages were noticed in the composites filled with modified and un-modified wood flour. In the first stage, the wood flour decomposition occurred from 335 to 350 °C. The second step de-polymerization and breakdown of the HDPE chain took place at or above 480 °C. The chemical modification influenced the thermal stability of the wood flour. The main decomposition temperature of the control samples was seen at 337 °C, while those of HDPE composites filled with modified wood flour were determined to be from 342 to 345 °C for MA, 348 to 350 °C for PA, and 348 °C for SA. It can be inferred from this result that the modified wood flour filled HDPE composites had little higher thermal stability. Ozmen *et al.* (2013) and Luz *et al.* (2008) reported that chemical modified wood flour/fiber in the polymer matrix increased thermal stability of the composites. In addition, all samples having wood flour had a residual weight between 0.71 and 6.28% at 500 °C.

### Scanning Electron Microscopy Analysis

Figure 4 shows the micrographs of HDPE composites filled with modified wood flour at 5% concentration and control samples. In Fig. 4a, detachment of the wood flour and cracks between the wood flour and HDPE occurred, which demonstrated that the un-modified wood flour and HDPE had a low interfacial binding force between them. It was also seen that the micrograph for control (un-modified) samples (Fig. 4a) had more gaps than those for maleic (Fig. 4b), propionic (Fig. 4c), and succinic (Fig. 4d) anhydride modified wood flour.

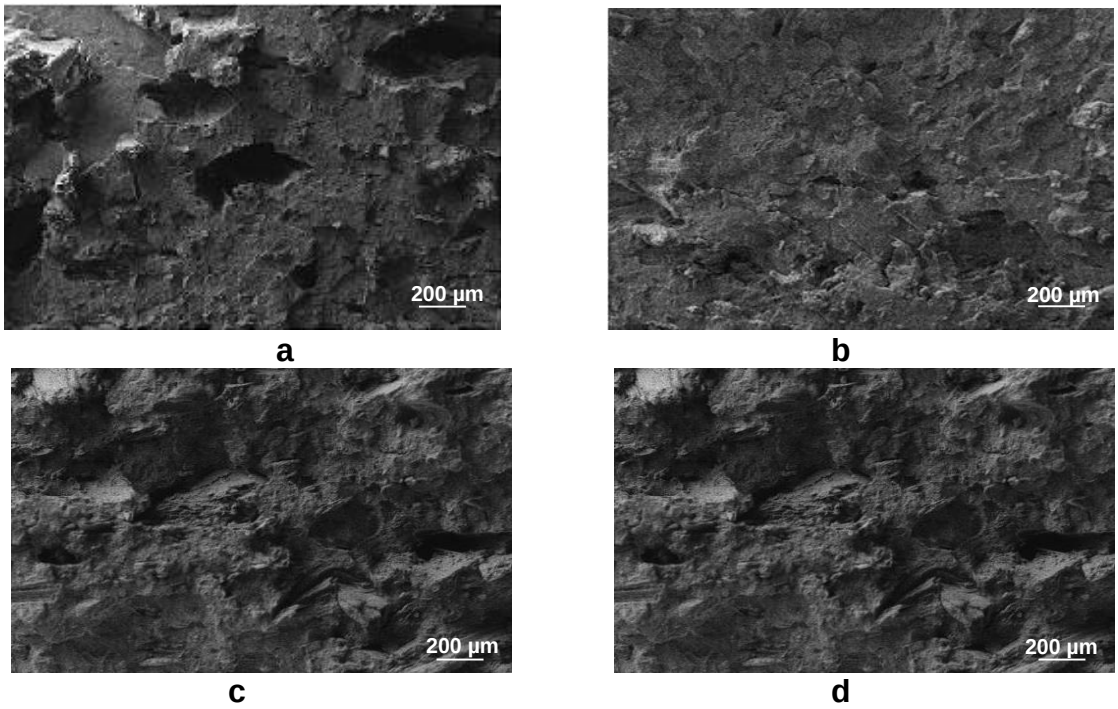



**Fig. 4.** Scanning electron micrographs of the HDPE composites filled with modified wood flour at 5% concentration. (a) Control, (b) maleic anhydride (M5), (c) propionic anhydride (P5), and (d) succinic anhydride (S5)

## CONCLUSIONS

1. Through modification, some of the mechanical properties (flexural strength, flexural modulus, and tensile modulus) were improved while some (tensile and impact strength) were not changed significantly.
2. The highest results for flexural, tensile, and impact strength were achieved with a 10% PA concentration. For the tensile and flexural modulus, 15% MA modified samples provided the highest results.
3. For the thermal properties, modification had a limited influence. Thermal stability was slightly improved. Performances of the modification types can be presented as MA < SA ≤ PA.
4. The LOI values were slightly improved and SA modification provided better LOI values compared to others.

## ACKNOWLEDGMENT

The authors would like to thank to Prof. Dr. Sibel Yildiz for her support during modification of wood flour.

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Article submitted: May 29, 2014; Peer review completed: August 1, 2013; Revised version received and accepted: August 30, 2014; Published: September 9, 2014.