THERMAL BEHAVIOUR OF POLYURETHANE MATRIX COMPOSITE MATERIALS

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ABSTRACT. This paper describes the thermal behaviour of some composite materials, polyurethane foams reinforced with tire rubber waste and fir sawdust. According to experimental results, TG and DTG plots were drawn for finding the thermal stability domains, the partial and total weight loss and the temperature of the maximum weight loss. Composite materials have superior thermal stability of raw materials from which they were made. Increasing the percentage of polyurethane foam results in greater weight loss front of recycled rubber, but lower than fir sawdust and polyurethane foam.

Keywords: thermal analysis, fir sawdust, polyurethane foam, recycled rubber

INTRODUCTION

Thermogravimetric analysis (TGA) is a thermal analysis technique which measures the amount and rate of change in the weight of a material as a function of temperature, in static rate or under a temperature program, in a controlled atmosphere.

TGA technique is becoming increasingly used not only in determining the composition of materials but also to predict their thermal stability up to elevated temperatures. In TGA, typical weight loss profiles are analyzed for the amount or percent of weight loss at any given temperature, the amount or percent of non-combusted residue at final temperature, and the temperature of various degradation steps [1, 2].

In the last decade, the incorporation of reinforcements from natural resources such as jute, sisal, hemp, kenaf and wood fibers into polymeric materials to improve their performance has been widely studied [3–8].

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Polyurethane foams are used in many applications such as automotive, bedding and furniture industry. This is explained by their exceptional characteristics such as sound insulation, energy and shock absorption, consumer comfort and protection from impact. However, polyurethane foam also has some disadvantages, such as low thermal stability and low mechanical strength [9–12].

Thermal degradation of wood is highly dependent on its constituents [13, 14]. The complex structure of wood and the interaction between its components makes it difficult to differentiate the degradation of each component (cellulose, holocellulose, hemicelluloses and lignin) on heat treatment.

The thermal behavior of materials containing wood [15–18], rubber [18, 19] and polyurethane foam [20, 21] is strongly dependent on the composition and interfaces established between components.

The main aspects on the thermal stability of polyurethane foam, fir sawdust, particles of recycled rubber and composite materials obtained from these raw materials, are presented in this study.

RESULTS AND DISCUSSION

For a more complex characterization of the new composite materials based on recycled rubber, fir fibers and polyurethane foam, a thermogravimetric analysis was necessary. Thermal stability of raw materials used to obtain composite materials is an important aspect for their fabrication process; its highest processing temperature being known. Thermal analysis can offer useful information on stability or the temperature range in which the compounds can be used without changing their composition and properties [22], and therefore for possible applications.

Thermal degradation of fir sawdust is dependent on its constituents, the small weight loss before 100°C can be attributed to water evaporation; weight loss rate gradually increased above 200°C and a distinct weight loss appeared between 200–400°C [15]. It is known that the hemicelluloses decompose before lignin and cellulose [16]. Kim et al. confirmed that hemicelluloses degrade between 180–350°C, the lignin degrades between 250–500°C, and the degradation of cellulose takes place between 275–350°C [17].

Thermal decomposition of rubber derived from waste tires is characterized by three distinct decomposition regions: the degradation or volatilization of additives such as oils and stearic acid (200–300°C); the degradation of natural rubber (NR) and styrene–butadiene rubber (SBR), which are the main components of tire rubber (350–480°C) and the decomposition of butadiene rubber (BR) (450–500°C) [18, 19].

The polyurethane foam exhibited three thermal decomposition steps at onset temperatures: the vaporization of any volatiles and unpolymerized medium molecular weight units of the resin component (135°C); the faction of the polyol-

isocyanate bond formed during polymerization where the vaporized isocyanate component and liquid polyol remained (290°C) and char formation from the pyrolysis of the polyol component (450°C) respectively [20, 21].

The temperature domains of the decomposition stages, for new composite materials, starting temperature of weight loss steps, partial and total weight loss and temperature of the maximum weight loss for all samples, are presented in Table 1.

Analyzing the data in Table 1 we can observe that weight loss for the analyzed raw materials is quite different, 66.1% for recycled rubber (R), 83% for fir sawdust (FS) and 94.4% for polyurethane foam (PUF). This behavior is expected and can be explained by the fact that there are different materials. In terms of thermal stability, R has the highest stability (T_{max}=458°C) followed by PUF (T_{max}=381°C) and the last one is FS (T_{max}=359°C). It is expected that the thermal behavior of the raw materials influence the thermal behavior of composite materials of which they are part.

Table 1. Thermal degradation temperatures and weight loss of the investigated samples.

Sample	Temperature domain [°C]	T_{onset*} [°C]	T_{max} [°C]	Partial weight loss [%]	Total weight loss [%]
Polyurethane foam (PUF)	25 - 330	253	320	15.3	94.4
	330 - 800	350	381	79.1	
Fir sawdust (FS)	25 - 150	45	63	4.0	83.0
	150 - 800	250	359	79.0	
Recycled rubber particles (R)	25 – 430	299	372	49.2	66.1
	430 – 800	435	458	16.9	
Recycled rubber and 10% polyurethane foam (R-PUF10%)	25 – 320	244	305	9.2	67.2
	320 – 430	331	379	37.7	
	430 - 800	435	460	20.3	
Recycled rubber and 20% polyurethane foam (R-PUF20%)	25 – 320	247	308	9.8	69.3
	320 – 430	340	381	40.5	
	430 - 800	439	457	19.0	
Fir sawdust, recycled rubber and 15% polyurethane foam (R-FS-PUF15%)	25 – 320	250	310	10.5	69.8
	320 – 430	339	388	33.5	
	430 - 800	429	458	25.8	
Fir sawdust, recycled rubber and 25% polyurethane foam (R-FS-PUF15%)	25 – 320	252	320	10.4	73.5
	320 – 430	349	395	37.1	
	430 - 800	437	461	26.0	

T_{onset*} = *starting temperature of weight loss steps.*

Figure 1 shows the TG curves, for composite materials made from particles of recycled rubber and polyurethane foam in different proportion. Total weight loss increases with the increase in the percentage of polyurethane foam used as binder, from 67.2% for sample R-PUF10% to 69.3% for sample R-PUF20%, compared to R 66.1%. Comparing the two composites in terms of thermal stability with raw materials, the sample R-PUF10% has a better thermal stability decomposed at 460°C instead of 458°C, the decomposition temperature for R.
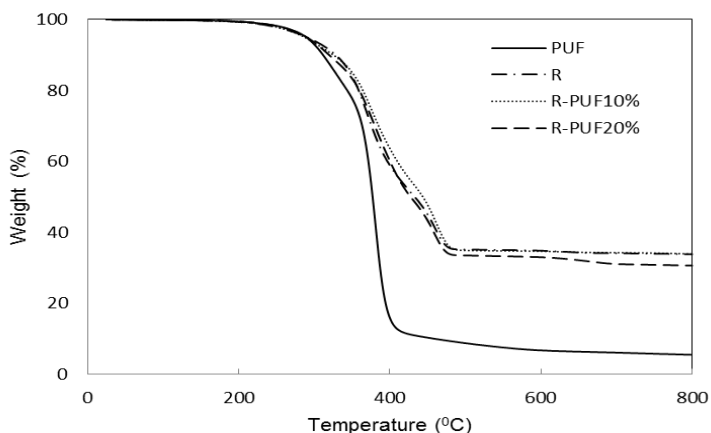
Figure 1. TG curves of the composite materials with rubber (R) and polyurethane foam (PUF)
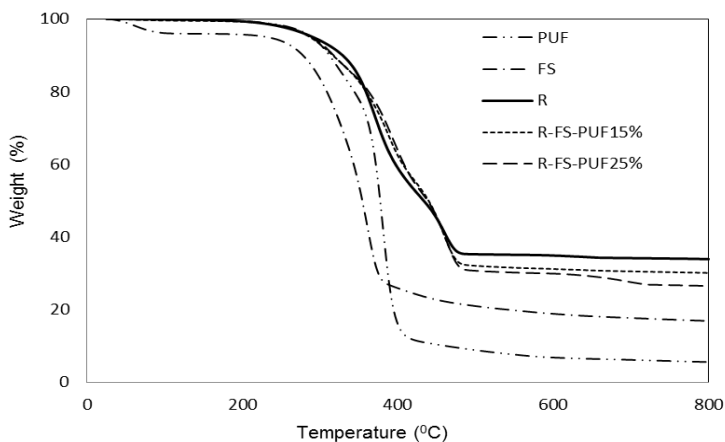

Figure 2. TG curves of the composite materials with rubber (R), fir sawdust (FS) and polyurethane foam (PUF)

For composite materials based on recycled rubber (25%) and fir sawdust (25%) and 15% respectively 25% polyurethane foam as binder, (Figure 2) total weight loss increases with the percentage of binder, from 69.8% to 73.5%, compared to the weight loss of the recycled rubber. The R-FS-PUF25% sample had a higher thermal stability, it decomposed at 461°C, with three degrees higher than major raw material R. In conclusion, the composite material has a better thermal stability than raw materials.

DTG curves, Figure 3, clearly showed that the recycled rubber had two distinct decomposition regions. The first weight loss (49.2%) was between 25–430°C, and was attributed to the degradation or volatilization of additives such as oils and stearic acid and to the degradation of natural rubber (NR) at 372°C. The final weight loss (16.9%) was 430–800°C and it appeared mainly due to the degradation of styrene–butadiene rubber (SBR) at 458°C, and butadiene rubber (BR) at 467°C. The observed degradation trend was in accordance with a former study which attributed the DTG peak temperature of 378°C to NR, 458°C to SBR and 468°C to BR [18].
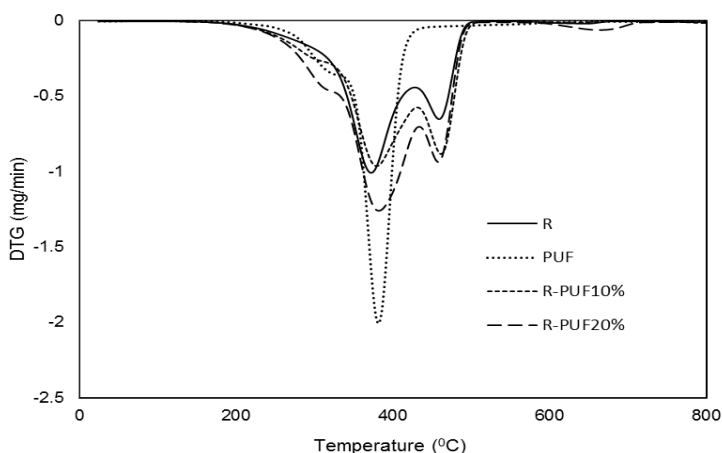

Figure 3. DTG curves of the composite materials with rubber (R)
and polyurethane foam (PUF)

In the cases of the composite materials, R-PUF10%, respectively R-PUF20%, if a mass loss occurs at around 247°C due to the scission of the polyol-isocyanate bond formed during polymerization, the weight loss of composite materials increases with the percentage of polyurethane foam used as binder (Figure 3).

On the decomposition curve of fir sawdust (Figure 4), the first peak appeared below 100°C and can be assigned to the evaporation of water. The second peak at 359°C was broad, which means there was overlapping between the decomposition of hemicelluloses, cellulose, lignin and wood extractives.
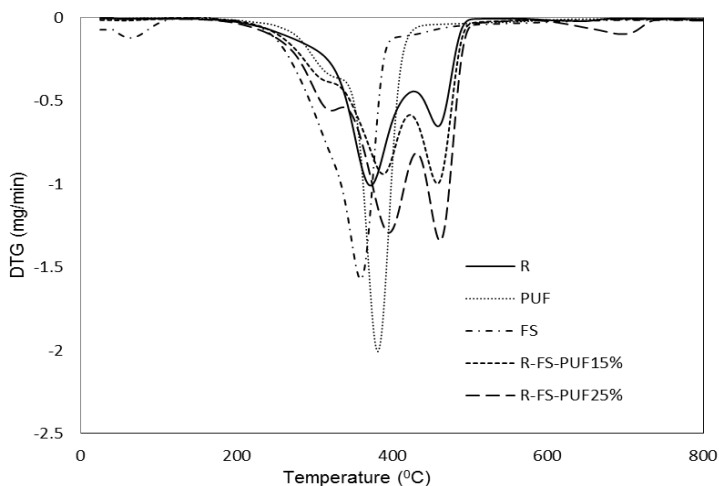
Figure 4. DTG curves of the composite materials with rubber (R),
fir sawdust (FS) and polyurethane foam (PUF)

The thermal stability of composite materials with fir sawdust added is better than that of the composite materials with recycled rubber and polyurethane foam only. In Figure 4 is observed that composite materials keep the shape of the recycled rubber decomposition curve, but with a greater weight loss and an increase in decomposition temperature.

CONCLUSIONS

The thermogravimetric plots show that basic research may be possible to describe the mechanisms of thermal decomposition of waste (fir sawdust and rubber from tires) and polyurethane foam, as raw materials.

Weight loss of analyzed raw materials is quite different, 66.1% for R, 83% for FS and 94.4% for PUF, because they are different materials but combined together in well-defined proportions give composite materials with superior properties.

Thermal stability of composite materials investigated are superior to any raw material use in this study and is clearly demonstrated by higher decomposition temperatures of composite materials: 461°C for R-FS-PUF25% and 460°C for R-PUF10% instead of 458°C for R 381°C for PUF and 359°C for FS, the decomposition temperatures of raw materials.

EXPERIMENTAL SECTION

Samples

Samples analyzed in this study are composite materials based on two types of raw materials (fir sawdust and recycled rubber particles from used tires) and polyurethane foam (flexible, with open cell) as binder.

Investigation methods

Thermogravimetric analysis (TGA) we performed on based composite materials with fir sawdust, polyurethane foam and recycled rubber particles, was performed using a Mettler-Toledo TGA/SDTA 851e, 1600°C, Analysis Thermal System.

Measuring conditions. Samples were placed in an alumina crucible and heated at 10°C/min over a temperature range of 25–800°C. The experiments were conducted under a nitrogen atmosphere at a flow of 50 mL/min. Samples weights of TGA were between 15–25 mg in their original state.

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