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THERMOGRAVIMETRIC ANALYSIS OF COMPOSITES OBTAINED FROM SINTERING OF RICE HUSK-SCRAP TIRE MIXTURES

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The disposal of used automotive tires has caused many environmental and economical problems to most countries. We propose the use of rice husk as filler for increasing the value of recycled tire rubber. Thermal degradation of both components and their sintering mixtures is presented in this paper. Thermal decomposition of rice husk occurs in various steps in the temperature range between 150 and 550°C. This complex process is the result of the overlapping of thermal decomposition of the three major constituents common in all lignocellulosic materials, i.e., hemicellulose, lignin and cellulose. Hemicellulose is degraded at temperatures between 150 and 350°C, cellulose from 275 to 380°C and lignin from 250 to 550°C. The degradation process of major constituents of scrap tires or their composites is observed at temperatures between 150 and 550°C. For composites, the addition of rice husk (maximum 25%) produces an increase in the mass loss rate. This effect is higher as the amount of rice husk increases. However, the degradation initial temperature of elastomeric matrix is not affected with addition of rice husk. Apparent kinetic parameters were also studied by the isoconversional Friedman method. We observed that the addition of rice husk produces a decrease in apparent activation energy for low conversions (up to 0.6). For higher conversions this decrease was not so clearly observed.

Keywords: *apparent kinetic parameters, rice husk, rubber composites, thermal degradation*

Introduction

The disposal of used automotive tires has caused many environmental and economical problems to most countries. Particularly, Spain produces 250,000 tons of tires per year, representing 63.9% of the total production of rubber materials. But, after its use, most of the scrap tires are dumped in open or landfill sites. As it is known, tires are mainly composed of rubbery materials in the form of C_xH_y with the addition of some fibrous materials. One of the main characteristics of rubber tires is their high volatile and fixed carbon contents with heating value greater than that of coal. But some environmental concern rose during the last years regarding the incineration of tire rubber [1]. Therefore, some efforts in the recycling of tires after its service period were recently carried out. Some recent studies have proposed the use of recycled tire rubber to produce thermoplastic elastomers [2]. However, despite promising results, this possibility seems to be very difficult for application in industrial use, as the resulting product is still too expensive. Therefore, the addition of another waste product for reducing costs seems necessary. The use of rice husk as filler for this purpose has been recently proposed [3, 4]. Rice husk is a cheap and abundant waste product from agriculture. The world rice production in 2003 was approximately 582 million tons. As a consequence, approximately 145 million tons of husk residues were produced. It is necessary, then, to consider the use of this residue in polymer formulations with a clear positive effect to the environment. The main components of rice husk are cellulose 32.7%, hemicellulose 20.5%, lignin 21.8%, silica 15.1%, solubles 2.8% and moisture 7.5% [5, 6]. These average values can change for different rice varieties.

Thermal decomposition of rice husk studied with thermogravimetric analysis (TG) occurs in various steps in the temperature range between 150 and 550°C. This complex process is the result of the overlapping of thermal decomposition of the three major constituents that are common in all lignocellulosic materials, as jute, wood, sisal, fique and bagasse [7–10]. Many works have focused their interest in the study of the mixing conditions between thermoplastic matrices and rice husk or rice husk ash and the mechanical properties of the composites [4, 11, 12]. On the other hand, some works have been carried out on the thermal stability of such blends or composites [12, 13]. In particular, we have studied the possibilities to obtain composites by sintering of recycled scrap tire – rice husk pow-

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der mixtures. Some preliminary results showed a promising behaviour regarding processing and mechanical properties [14]. In this work we will focus on the modification of these materials, in particular on all aspects related to the thermal stability of composites and the effects of interaction between rice husk and scrap tire on the thermal degradation process.

Experimental

Materials

The scrap tire powder was supplied by Insaturbo SA (Alicante, Spain). A previous separation treatment was carried out in order to eliminate steel and other fibers used in tires manufacturing. The sample was then sieved during 30 min. Table 1 shows the size distribution of powder particles with a maximum for a size fraction of 250 μm. Rice husk used in the present work was collected from Cooperativa Arrocera Sarmiento in Concepción del Uruguay, Entre Ríos (Argentina). The sample was grounded using an analytic mill (IKA 50, Ika-Werke GmbH and Co. KG, Staufen, Germany) during 10 min. Then, the sample was sieved during 10 min with a 250 μm sieve, selecting the size fraction minor to 250 μm.

Samples preparation

Samples were prepared in 22×20×0.4 cm plates by sintering of tire powder modified with different amounts of rice husk powder (0, 5, 10, 15, 20 and 25 mass%). The sintering was carried out in a home-made heating press with the following heating program: From room temperature to 170°C at 10°C min^{-1}, maintaining this temperature during 10 min (1 MPa pressure).

Thermogravimetric analysis

Dynamic degradation measurements were carried out using a Mettler-Toledo 851^e-TGA-SDTA system (Schwarzenbach, Switzerland) coupled to STAR-E software. Tests were performed in dynamic mode in order to cover a wide range of thermal conditions in a nitrogen environment (flow rate 200 mL min^{-1}). TG tests were performed in alumina crucibles (5.9×4.7 mm) where samples were placed without any previous treatment and experiments were run immediately. The sample mass in all tests was approximately 10 mg. Temperature programs were run from 30 to 750°C at heating rates between 2, 5, 10, 15, 20, 25 and 30°C min^{-1}. Data obtained from TG experiments were transformed in ASCII format and analyzed using a statistics computer program.

Results and discussion

Thermal degradation of rice husk

Figure 1 shows the typical normalized dynamic TG and derivative (DTG) curves for the pyrolysis of rice husk powder in nitrogen atmosphere (dashed line). As can be observed, thermal decomposition of rice husk occurs in the temperature range between 183 and 538°C for a heating rate of 20°C min^{-1}. This process is the consequence of the superposition of the degradation of the three major constituents, which are common in all lignocellulosic materials, i.e., hemicellulose, lignin and cellulose. Hemicellulose is degraded at temperatures between 150 and 350°C, cellulose from 275 to 380°C and lignin from 250 to 550°C [5, 6, 15, 16]. But, as usual in all activated process in TG tests, these parameters change as a function of the heating rate. In the case of the DTG curve normalized with the heating rate of rice husk (Fig. 2), the superposition of the thermal curves of each component leads to the formation of a peak corresponding to cellulose (311 and 360°C for heating rates of 2 and 30°C min^{-1}, respectively), the peak at lower temperature corresponding to hemicellulose (291 and 318°C for heating rates of 2 and 30°C min^{-1}, respectively) and a broad peak at higher temperatures corresponding to lignin, which is completely overlapped by the other two. Another factor observed at

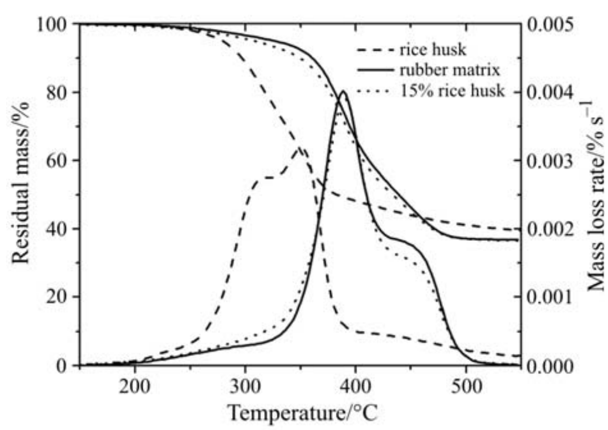

Fig. 1 Mass loss rate and residual mass percentage at 20°C min^{-1}; -- – rice husk, ··· – scrap tire modified with 15% rice husk and — – scrap tire

Table 1 Size distribution of scrap tire powder

Size mesh/mm	2	1.25	1	0.50	0.25	0.125	0.1	0.063
Amount of scrap tire/%	0.2	0.4	0.85	35.9	43.5	18.7	0.40	0.05

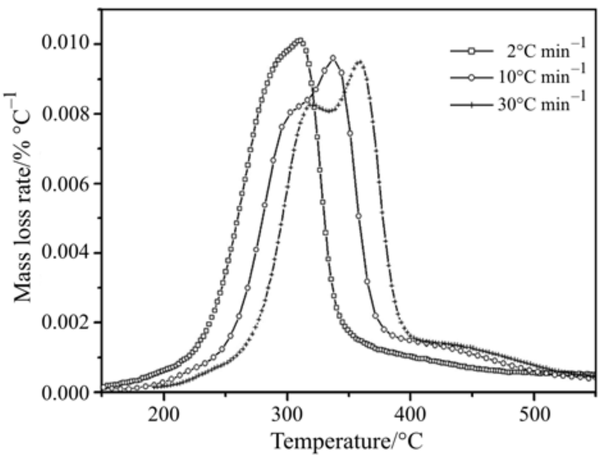

Fig. 2 Variation of mass loss rate with temperature for rice husk at different heating rates

different heating rates is the decrease of the overlapping between hemicellulose and cellulose peaks when the heating rate is raised leading to a higher definition of TG curves. Degradation temperatures (both, initial and final) are usually function of the heating rate and atmosphere used for the analysis. Results reported by Mansaray *et al*. [15, 16] in nitrogen atmosphere show a decrease in the initial degradation temperatures for higher heating rates and different rice husk varieties. However, recent observations [6] as well as the results shown in Table 2, show a different tendency, indication of a thermally active process.

On the other hand, the difference between temperatures of maximum mass loss from hemicellulose and cellulose ranges from 20 to 42ºC with heating rate (from 2 to 30ºC min^{-1}), as observed in Table 2. Moreover, the mass loss percentage decreases slightly but significantly (65.5 to 62.6%) from low to high heating rates.

Thermal degradation of scrap tire

Dynamic TG and DTG curves for the thermal degradation of the scrap tire used in this study for a heating rate of 20°C min^{-1} are also shown in Fig. 1. DTG curve shows different regions for the whole temperature range between 150 and 550°C. These differences are the consequence of the degradation of each major constituent of rubber tires, such as natural rubber, butadiene rubber, styrene–butadiene rubber, as well as minor constituents such as oil, plasticizers, additives, moisture, etc. In the low temperature range (between 150 and 350°C) all the minor constituents are lost, as they are normally volatiles. The degradation process of major constituents or their combinations occurs between 340 and 550°C. It was previously indicated that the maximum mass loss of styrene–butadiene rubber occurs at 372 and 429ºC, maximum degradation of natural rubber at 373°C and for butadiene rubber at 372 and 460°C [1, 17, 18]. However, in the case of rubber combinations like those used in tires, it is observed that the mass loss for each peak in the DTG curves is dependent on the composition of the mixture. In spite of the relative homogeneity of the scrap tire used in this work, different compositions as a function of the relative amount of each elastomer are observed. We obtained similar values to those reported by Leung for temperatures and mass losses (for the same heating rates), indicating that the analyzed tire rubber have a similar composition [1].

Heating rate of the TG test influences both, the characteristic temperatures of the scrap tire thermal degradation and the shape of peaks. Initial and final temperature of the degradation process as well as the temperature of both characteristic peaks increases with heating rate (Table 3). However, differences between temperatures of maximum mass loss for both peaks are negligible at different heating rates.

Thermal degradation of composites

Figure 3 shows DTG curves for different rice husk-scrap tire composites (20°C min^{-1}). As can be observed, the addition of growing amount of rice husk to the composites produces an increase in the mass loss rate to low temperatures. This effect is more pronounced as the amount of rice husk increases, since for this temperature range rice husk shows the maximum of its degradation. It is also possible to distinguish the

Table 2 Variation of initial temperatures (T_I), final temperatures (T_F), hemicellulose peak temperature (T_{P1}) and cellulose peak temperatures (T_{P2}) with heating rate

Heating rate/°C min^{-1}	T_I/°C	T_{P1}/°C	T_{P2}/°C	T_F/°C	Total mass loss/%	(T_{P2}–T_{P1})/°C
2	150	291	311	487	65.50	20
5	152	295	325	501	63.14	30
10	166	307	338	521	62.58	31
15	172	314	345	526	62.92	31
20	183	316	352	538	62.70	36
25	192	317	355	549	62.21	38
30	194	318	360	550	62.59	42

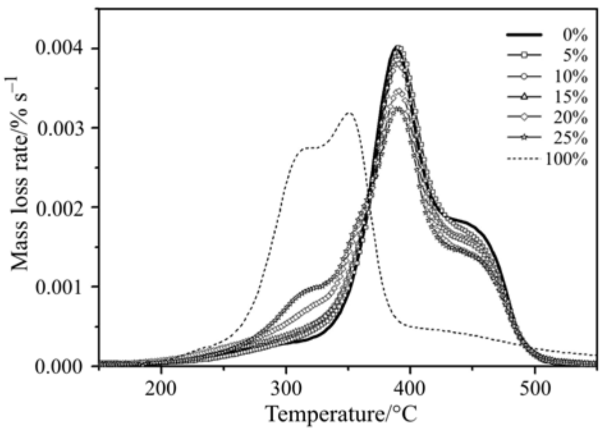

Fig. 3 Variation of mass loss rate with temperature for scrap tire samples modified with different amount of rice husk (20°C min^{-1})

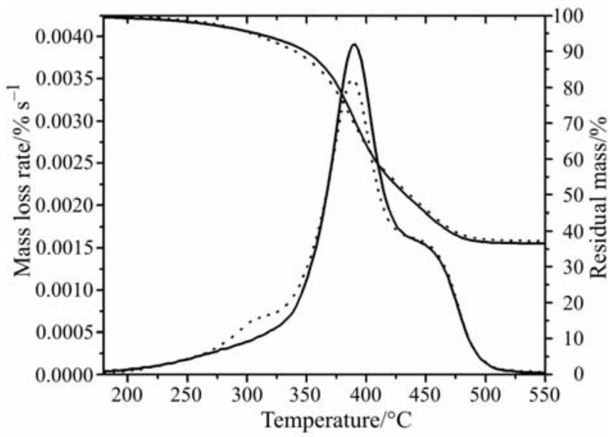

Fig. 4 Mass loss rate and residual mass percentage at 20°C min^{-1} of scrap tire modified with 15% rice husk, — – experimental curves, ··· – calculated from Eq. (1)

peaks corresponding to hemicellulose and cellulose (316 an 352°C, respectively) for samples with high contents of rice husk (between 15 and 25 mass%), but always overlapped by the decomposition of rubber. From 360°C to the final temperature in the tests, the addition of rice husk results in a decrease in the mass loss rate compared to unmodified rubber, independently from the heating rate. However, no significant effects are observed on peak temperatures and degradation initial temperatures for the composites (Table 3).

But, as usual in solid mixtures, interactions between both components are another point to be considered. In the case of no interaction between both materials the following equation is valid [19]

$$W_{MIX}(T) = f_{RH}W_{RH}(T) + f_R W_R(T) \quad (1)$$

where $W_{RH}(T)$ and $W_R(T)$ are normalized mass of pure materials, rice husk and rubber, respectively, at any temperature T. $W_{MIX}(T)$ is the normalized mass of the mixture of rice husk with mass fraction f_{RH} and rubber with mass fraction f_R at any temperature T.

Curves with data calculated according to Eq. (1) and experimental are plotted in Fig. 4 for a 15% rice hush materials at 20°C min^{-1}. It must be considered that rice husk particles are included inside the rubber matrix in the test sample. Results obtained from Eq. (1) predicted a higher mass loss rate for theoretical than experimental data from 250 to 350°C, where the main degradation of rice husk takes place. Similar behavior was observed for all mixtures with different percentages and heating rates. The main gaseous products of the pyrolysis of rice husk are CO and CO_2, as usual in cellulose products [19]. The inclusion of particles of rice husk in the rubber matrix produces a delay in the formation of gaseous products and consequently in the degradation of rice husk in the elastomeric matrix. This fact leads to an overall stabilization of the composites at the initial stages of the process.

Calculation of kinetic parameters

A complete thermal characterization of this system should be carried out by calculation of apparent kinetic parameters for the thermal degradation of scrap tires – rice husk composites. In order to analyze the effect of the addition of rice husk on the thermal decomposition of rubber, the classic isoconversional Friedman method was used [20]. This method consists of plotting ln(dx/dt) as a function of 1/T, for each x at a different heating rate (β) and a straight line with slope $-E_a/R$ is obtained. Results obtained for the calculation of apparent activation energies (E_a) for rice husk, rubber matrix and different composites for conversions between 0.1 at 0.9 are shown in Fig. 5. Independently of the variation of E_a with conversion degree for unmodified scrap tire (possibly due to the above-indicated interaction between components), the presence of rice husk produces a slight decrease in

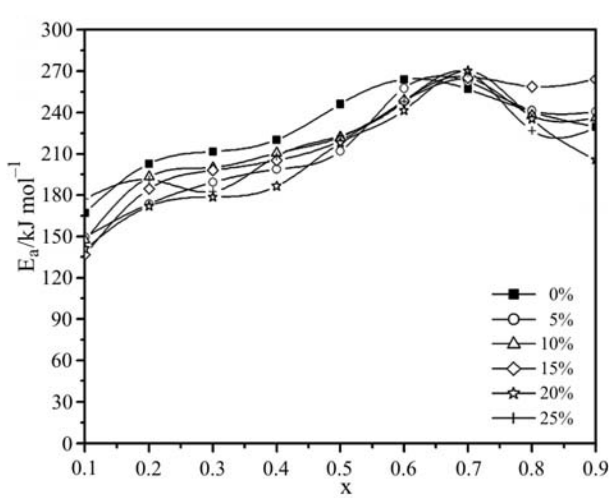

Fig. 5 Variation of apparent activation energies with conversion for rice husk-scrap tire composites

Table 3 Variation of initial temperature (T_I), final temperature (T_F), low temperature peak (T_{P1}) and high temperature peak (T_{P2}) with heating rate for the composites

Rice husk/mass%	Heating rate/°C min^{-1}	T_I/°C	T_{P1}/°C	T_{P2}/°C	T_F/°C	Total mass loss/%	(T_{P2}–T_{P1})/°C
0	2	152	349	405	469	62.12	56
	5	159	365	421	485	62.51	56
	10	177	377	434	505	62.87	57
	15	190	381	442	512	63.65	61
	20	191	389	446	520	63.20	57
	25	204	392	451	521	63.12	59
	30	207	397	455	528	63.66	58
5	2	150	350	404	469	62.90	54
	5	156	363	420	487	62.74	57
	10	175	378	435	508	63.84	57
	15	183	385	444	511	63.58	59
	20	188	391	452	522	63.94	61
	25	203	395	451	526	63.44	56
	30	200	397	455	525	63.55	58
10	2	149	349	404	469	63.50	55
	5	157	365	419	488	63.01	54
	10	168	379	435	507	61.93	56
	15	182	386	442	517	63.40	56
	20	186	389	451	521	62.79	62
	25	193	394	454	528	63.15	60
	30	198	396	457	529	63.52	61
15	2	149	350	402	467	66.04	52
	5	156	366	422	491	63.91	56
	10	174	378	436	508	63.65	58
	15	181	386	442	517	63.40	56
	20	184	390	450	526	63.48	60
	25	191	394	456	528	63.36	62
	30	200	397	458	530	63.46	61
20	2	150	349	403	468	67.83	54
	5	153	365	418	487	62.80	53
	10	164	377	430	502	59.99	53
	15	178	387	439	515	62.33	52
	20	180	391	448	525	63.11	57
	25	187	394	453	532	63.27	59
	30	198	396	457	528	59.60	61
25	2	149	349	405	467	64.66	55
	5	150	364	424	484	60.71	60
	10	167	378	438	508	62.82	60
	15	177	384	439	514	62.33	55
	20	184	391	448	524	63.28	57
	25	192	394	456	535	62.59	62
	30	195	395	454	529	63.09	59

E_a as the amount of rice husk increases for low conversions (up to 0.6). The lower E_a in the composites compared to values for unmodified scrap tire explains the higher mass loss rate in the initial stages of degradation as observed in Fig. 3. But, no other significant differences are observed for the addition of raising amounts of rice husk when compared to the values for E_a of scrap tire with no additions.

Conclusions

The addition of different amounts of rice husk (up to 25 mass%) to scrap tire rubber from recycling, results in composites with no differences at initial stages with the thermal processes associated to each component. Nevertheless, once the degradation process is initiated, the mass loss rate increases with the addition of rice husk. This fact does not represent a major drawback for the use of these composites for the manufacturing of some low value products. A comparison between experimental and calculated data from individual components shows a slight delay in the degradation process of rice husk in the rubber matrix. The final conclusion of this study is the validity of the use of these composites, which means the increase of the added value for two materials which are currently considered waste products and have no industrial re-use possibilities.

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