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Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres

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Abstract

The thermal degradation and fire resistance of different natural fibre composites were studied. Unsaturated polyester (UP) and modified acrylic resins (Modar) were used as matrix composites. The smoke emission of the materials was also analysed, as well as, the performance against the fire of the biocomposites and glass reinforced composites was compared. Thermal degradation indicated that the Modar matrix composites were more resistant to temperature than the composites with UP matrix. Flax fibre, due to their low lignin content, exhibit the best thermal resistance among the natural fibres studied.

From the results obtained about the thermal and fire resistance of the composites it is possible to conclude that the flax fibre seems to be the most adequate to be used, due to the long time to ignition and the long period prior to reach the flashover. On the other hand, the jute fibre composites showed a short duration but a quick growing fire with the lowest smoke emission. The low smoke is an important advantage, which reduces one of the main hazards of fire.

Keywords: Unsaturated polyester; Natural fibres; Thermal degradation; Fire resistance; Smoke emission

1. Introduction

Unsaturated polyester matrix composites have been used for many years in a broad technology fields such as naval construction, offshore applications, waterlines, building construction. Unsaturated polyester is an economical thermoset material that is widely used due to its excellent process ability and good crosslinking tendency as well as mechanical properties when cured [1,2]. Particularly, natural fibre reinforced polymers are used in the automotive and construction industry [3–6] because natural fibres exhibit many advantageous properties such as low weight, low cost, low density, high specific properties and availability from renewable resources. In a previous work [7] the mechanical properties of unsaturated polyester composites reinforced with different natural fibres (sisal, jute and flax) and glass fibre were evaluated. It was found that jute composites showed the best flexural and tensile strength values but the lowest impact results as a consequence of the higher interface adhesion. On the other hand, sisal fibre composites showed the lowest mechanical and water resistance properties. Woven jute and non-woven flax

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composites showed similar tensile and flexural properties, and also water absorption rate. Besides the mechanical properties and low cost it is important to evaluate the fire behaviour of a material for structural applications.

The cone calorimeter has been widely used for assessing the flammability of polymer materials and it has proven to be an useful device [8]. The technique is particularly useful for measuring heat release rate (HRR), total heat released (THR), time to ignition (TTI), smoke emission (SEA – specific extinction area) and average CO and CO_2, which represent the most important parameters to characterize fire [9,10].

When a material burns it generates heat, heating up and igniting additional combustible material. The material decomposes with the evolution of a flammable gas mixture. The ignition of the gas causes a highly and explosive rate of fire spread over the entire area. This point is called "flashover" which leads to the fully developed fire. The temperature exceeds 1000 °C and the fire spreads to the neighbouring areas. Then, the fire enters the decreasing phase depending on the size of the fire load and the ventilation conditions. The instant at which flashover occurs is of prime importance for the fire situation since it leads to the fully developed fire. At this stage the fire situation can no longer be controlled. Prior to flashover, the fire can be effectively fought in the vicinity of the initiating fire and extinguished. Determination of the rate of heat release from a material in a fire situation is important because of its influence on the initiating fire.

The secondary fire effects, smoke and toxic fire gases, occur alongside these phenomena, particularly as the rate of flame spread and heat released increases. Together with radiant heat and lack of oxygen they represent the greatest danger to people. Smoke and toxic gases have become increasingly important hazards because synthetic materials have been used most extensively in appliance manufacture. More than 50% of the victims succumbing at a fire die of smoke and toxic gas inhalation, not from direct fire or burns [8]. While carbon monoxide is the primary cause of death in accidental fires, the first response of an individual in a fire environment should be to try to escape. The visibility loss caused by the smoke limits the egress of the persons from the fire scenario. Smoke is a total occupancy hazard in the pre-flashover fire environment, not a localized problem. So, selection of materials based on a reasonably supported criterion of smoke generation can improve the time to escape potential in accidental fire [11]. The most desirable of these approaches would appear to be those which minimize the generation of combustible species, such as through increased polymer stability or char formation. This not only contributes to the reduction of visible smoke, but also tends to reduce flammability and limit the volume of combustion products formed [12].

The aim of this work was to evaluate the thermal degradation, fire resistance and smoke evolution of different natural fibre composites and glass fibre composites with the same matrix.

2. Experimental

2.1. Materials

Unsaturated polyester (Aropol FS 6912, from Ashland Chemicals) and unsaturated polyester with acrylic acid (Modar 835 S, from Ashland Chemicals) were used as matrices of the composite materials.

Woven jute (Castanhal Textil CIA, Brazil), mat flax (Finflax, Finland) and sisal (Brascorda, Brazil) were used as natural fibre-reinforcements. Non-woven glass mat (Vetrotex, Argentina) was used as reinforcement of the glass fibre composite.

The composites were obtained by a vacuum infusion technique. The resin enters through two injection points which are located in the corners of the mould and then it flows to the centre of the mould [7].

The volume percent of the fibres was 30%. The composites were cured at 60 °C during 2 h, and post-cured 3 h at 110 °C.

2.2. Methods

Thermogravimetric analysis (TGA) was carried out on the composites by means of a Shimadzu thermal analyser at a heating rate of 10 °C/min under nitrogen atmosphere.

The composite materials were tested in an ATLAS cone calorimeter to obtain their heat release rate (HRR) and smoke evolution characteristic. ISO 5660: 1993 was taken into account for the test measurements. The samples were tested in horizontal configuration. The radiant heat flux was 35 kW/m^2 on the specimen, which has an exposed surface area of 0.010 m^2 (100 mm × 100 mm). The measured exhaust gas flow was 0.023 m^3/s. The thickness of the specimen was 4 ± 0.2 mm.

3. Result and discussions

3.1. Thermal degradation by TGA

The degradation behaviour of the different natural fibres was studied by TGA (Fig. 1). In natural fibres, the degradation involves two main steps. The first one is the thermal depolymerisation of the hemicellulose and the cleavage of glycosidic linkages of cellulose and the second one is related to the decomposition of the α-cellulose [13–14]. The decomposition of the lignin

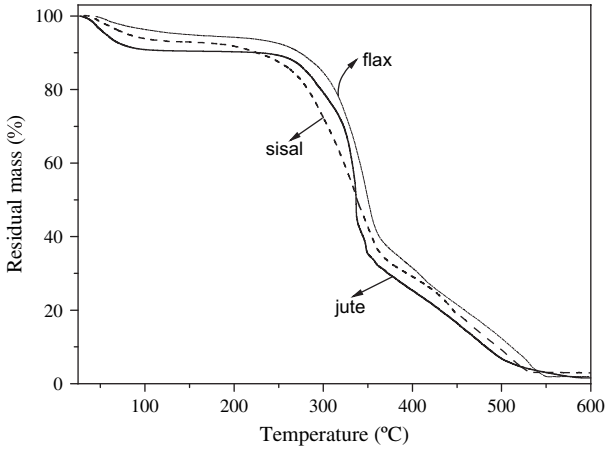

Fig. 1. TGA curves of the natural fibres.

takes place in a broad range of temperature, between 200 and 500 °C [15]. Fig. 2 shows the derivative of the residual mass percentage (DTG) for the different fibres studied. In sisal fibres the decomposition starts at 215 °C with a slight that could be assigned to the lignin degradation. The maximum degradation rate takes place during α-cellulose decomposition at 340 °C. The decomposition of the hemicellulose appears as a shoulder of the main peak at 290 °C. This result is in line with the observations of other authors [13,14,16]. Jute fibres decompose in the same way as sisal fibres, but the lignin degradation cannot be seen in the DTG curve probably because it is overlapped with the hemicellulose and α-cellulose decomposition.

Flax fibre starts to degrade at higher temperatures, with the main peak at 345 °C and a small shoulder corresponding to the hemicellulose at 285 °C. The results obtained for jute and flax fibres agree with those obtained by Dash et al. [17] and Wielage et al. [18],

Table 1
Chemical composition of the different natural fibres used in this work [19]

Component [%]	Jute	Flax	Sisal
Cellulose	64.4	64.1	65.8
Hemi-cellulose	12.0	16.7	12.0
Pectin	0.2	1.8	0.8
Lignin	11.8	2.0	9.9
Water soluble substances	1.1	3.9	1.2
Wax	0.5	1.5	0.3
Water	10.0	10.0	10.0

respectively. The better thermal stability (considering the thermal stability as the temperature needed to start the degradation) of the flax fibres could be put down to their lower lignin content (Table 1). During thermal decomposition of lignin, relatively weak bonds break at lower temperature whereas the cleavage of stronger bonds in the aromatic rings takes place at higher temperature [20]. Thus, with a lower lignin content, the degradation begins at a higher temperature, but the fibres do not have the oxidation resistance given by the aromatic rings in the lignin [21,22].

Fig. 3 shows the residual mass and DTG curves for UP and Modar resins. UP resins degrade by statistical chain rupture in which styrene is the primary product [23]. The Modar matrix exhibits a higher thermal resistance than the unsaturated polyester (Fig. 3) due to the content of acrylic acid. Also, the percentage of residual mass at the final of the test is higher for the Modar matrix indicating that it forms a charring structure.

Fig. 4 shows the residual mass percentage curve for the glass and jute composites with polyester and Modar matrix. As it was expected, the glass fibre improves the thermal resistance of the composite and gives a charring structure at the end of the test.

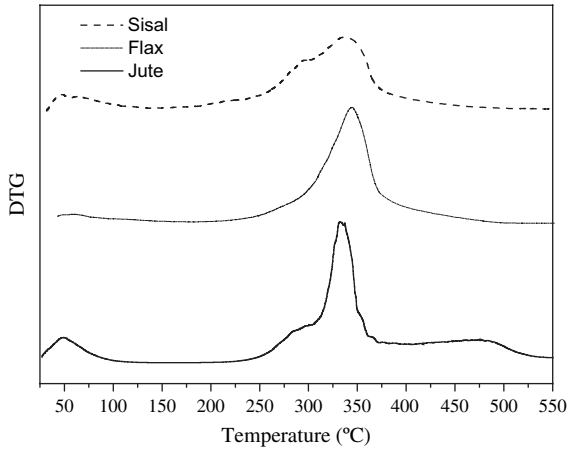

Fig. 2. DTG curves for the natural fibres.

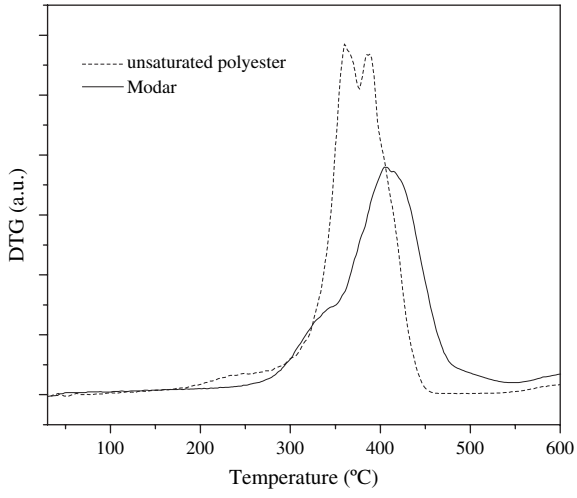

Fig. 3. DTG curves for the resins.

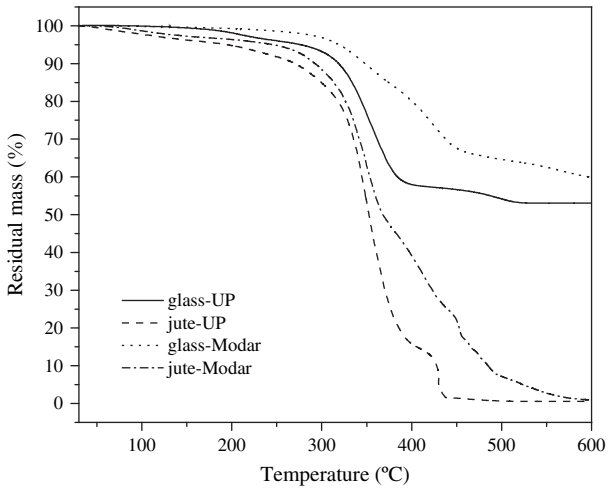

Fig. 4. TGA curves of the jute and glass composites.

The Modar matrix composites show a higher thermal resistance than the composites with polyester matrix. This is due to the higher resistance to temperature of the Modar matrix (Fig. 3).

3.2. Decomposition and smoke emission by cone calorimeter

3.2.1. Modar–fibre composites

Fig. 5 shows the HRR as a function of the time for the composites with the different natural fibres studied and Modar resin as matrix. All of these HRR curves show a first peak, which indicates the start of burning and after this peak the HRR drops due to the formation of an insulating char layer [9,24] from the Modar resin. The second peak arises because the temperature increases on the unexposed surface with the complete destruction of the charred material. Obviously, there is a strong decrease in the HRR when the material is consumed. By comparing the HRR curves in Fig. 5 the flax composite curve starts to burn later than the other composites and has a large flashover zone. This parameter indicates that it should be the more suitable natural fibre composite, among the studied, because it shows the longest time available to escape or to extinguish the fire due to the extensive flashover zone. The time to ignition and the total heat evolved for the same composites were determined (Table 2).

Table 2
Time to ignition of the composites with Modar matrix

Matrix	Fibre in the composite	Time to ignition (TTI) (s)	Total heat evolved (MJ/m^2)
Modar	Glass	62	54.4
	Flax	110	104.9
	Sisal	52	101.4
	Jute	72	74.2
Unsaturated polyester	Glass	56	32.3
	Jute	51	77.6

The results in Table 2 show that the total heat evolved is high for the flax fibre composite but it has the longer time to ignition. This could be due to their low lignin content as it was mentioned before (Table 1). As all the factors mentioned lead to different behaviours of the composites against the fire, the fire risk, which joins these three factors given the performance against the fire of the materials, was analysed. The fire risk was obtained by plotting the total heat evolved against the peak of the heat release rate divided by time to ignition [25]. The results for the fibre composites studied are shown in Fig. 6. The *y*-axis indicates the propensity to cause a fire of long duration, and the *x*-axis illustrates the propensity to cause a quickly growing fire. From Fig. 6 it follows that the three natural fibres studied

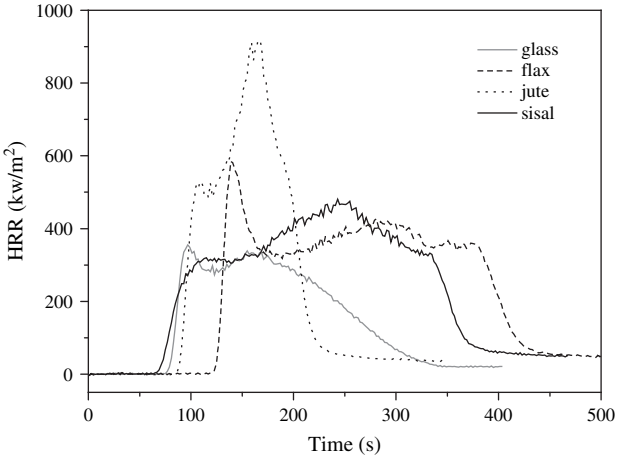

Fig. 5. HRR of the fibre composites with Modar matrix.

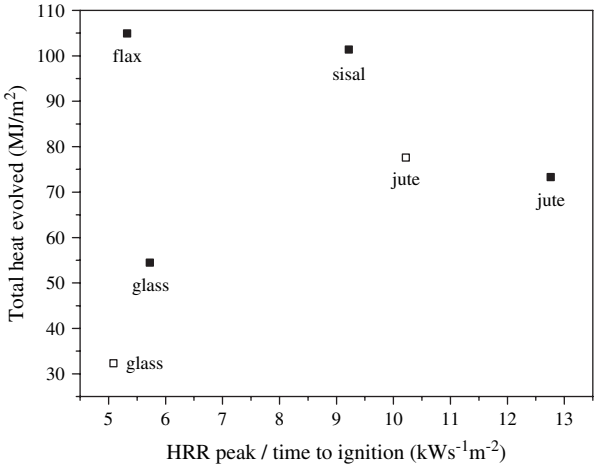

Fig. 6. Fire risk of the natural fibre composites with: (■) Modar matrix and (□) polyester matrix.

show a different behaviour against fire. The composites containing flax and sisal fibres cause a longer duration but slow growing fire. Instead, jute fibre composite causes a quickly growing but short duration fire (it was also observed in the HRR curves). The glass fibre composite, as was expected, is the one that shows a minor fire risk.

The same behaviour could be seen in the percentage of residual mass in the cone calorimeter tests (Fig. 7). The composite with jute fibre loses its mass faster than the other composites and reaches the final constant value at approximately 200 s. Sisal composite begins degradation earlier than the flax composite and both reach constant weight after approximately 350 s. The mass loss rate is similar for the last two composites.

Another parameter that should be analysed is the fire hazard, which is related to the CO and smoke evolution. Loss of visibility due to heavy smoke can hinder escape until toxic gas concentrations and temperatures become critical. Reduction in the rate or intensity of visible smoke development will help to increase escape time [12]. Table 3 shows the CO and CO_2 evolution. The results are similar for the natural fibre composites studied probably due to the similar composition of the natural fibres, although jute fibre exhibits a slightly lower CO emission. In addition, jute fibre composite exhibits highest emission of CO_2 among the natural fibre composites studied. The CO_2 acts as flame-extinguishing agent and as a diluent for combustible gas [26] and perhaps it contributes to the short duration fire of the jute fibre composite.

The glass fibre composite shows the highest CO and CO_2 evolution. This could be probably because the glass fibre as reinforcement of unsaturated polyester has been found to change the crosslinking density and to increase the quantity of degradation products [27] with emission of black smoke in considerable amounts [28].

Table 3
Average SEA, CO and CO_2 evolved of the composites with Modar and unsaturated polyester matrices

Matrix	Fibre in the composite	Average SEA (m^2/kg)	Average CO (kg/kg)	Average CO_2 (kg/kg)
Modar	Glass	491.60	0.0271	2.0457
	Flax	460.70	0.0219	1.8559
	Sisal	432.87	0.0206	1.8423
	Jute	225.50	0.0162	1.9129
Unsaturated polyester	Glass	709.49	0.0418	1.9028
	Jute	736.11	0.0409	1.7618

It has been demonstrated that both the intensity and rate of development of visible smoke can be important factors in assessing fire survivability [12]. The specific extinction area (SEA), that is defined as smoke evolved per mass unit of volatile produced upon heating [29], was calculated. The SEA represents the relationship between the volatile property and smoke emission. The average SEA results are shown in Table 3. It has been seen that jute fibre composite releases lower quantities of smoke from volatiles than the other composites. This is because the flax used was in the mat form and it is more difficult to degrade than the other fibres in spite of the similar composition. Previous results [7] of a flame test made on similar materials indicated that the composite with jute fibres was the sample with higher dimensional stability after burning.

3.2.2. Unsaturated polyester–fibre composites

For comparison purpose, composites with unsaturated polyester matrix reinforced with jute and glass fibres were analysed by means of a cone calorimeter. Fig. 8 shows the HRR curves and Table 2 shows the ignition time and total heat evolved for these composites. The HRR curves show a pre-ignition period, then a rapid

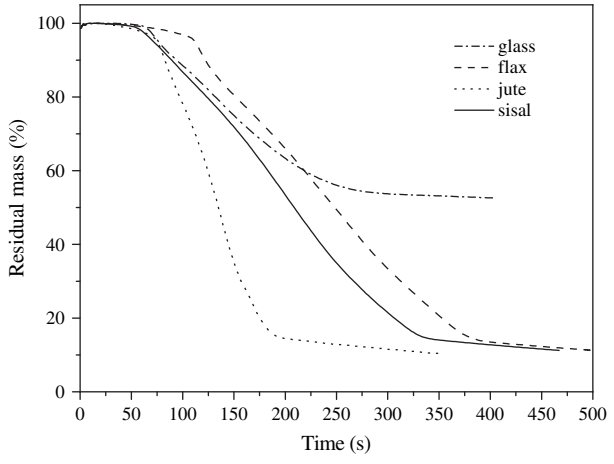

Fig. 7. Percentage of residual mass of the natural fibre composites with Modar matrix.

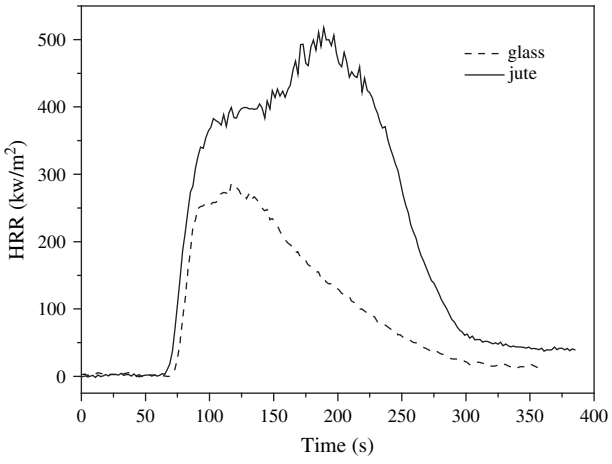

Fig. 8. HRR of the polyester matrix composites.

rise, followed by a short steady state before the second peak. The absence of the decrease after the first peak indicates that the unsaturated polyester resin does not form a charring structure as Modar does. The glass fibre composite exhibits better performance against fire. The times to ignition are longer for the Modar matrix composites than for the polyester matrix composites (Table 2).

As in the case of Modar matrix composites, the fire risk was calculated for the unsaturated polyester–fibre composites. The results are included in Fig. 6. By comparing the values obtained for the composites made with the two different matrices, the results show that the unsaturated polyester composites exhibit a slightly lower fire risk than the Modar composites. However, the composites with Modar matrix show a longer time to ignition than the unsaturated polyester matrix composites.

The smoke hazard of fire was also evaluated for the polyester matrix composites. The SEA average values (Table 3) are higher for the polyester matrix composites. The amount of CO and CO_2 evolved for the glass and jute composites with polyester matrix was determined (Table 3). These results were compared with those obtained for the Modar matrix composites and was observed that the polyester composite evolves approximately twice of CO than the Modar composite. It was demonstrated that smoke generation can be significantly reduced by replacing the polystyrene bridges with non-aromatic bridges [23]. Similarly, the char forming materials as Modar composites, form limited amounts of smoke [12]. The amount of CO_2 released was similar for both matrices. These results indicate that the smoke hazard of fire is more serious for the UP composites.

4. Conclusions

From the data obtained in the cone calorimeter tests, the composites were ranked according to their performance in terms of fire risks and smoke hazards of fire. Among the composites with Modar matrix, the one reinforced with sisal fibre showed the highest fire risk and in global terms the worst fire resistance. Jute fibre composites showed a quick growing but short duration fire and, conversely, flax fibre composite developed a long duration but slow growing fire. Glass fibre composites showed more flame resistance than the biocomposites. However, higher emission of CO and CO_2 was observed. This could be a consequence of the presence of an inert reinforcement in the composite, that reduces the crosslinking density of the matrix, giving chains with lower molar mass that can be easily degrade into CO and CO_2.

Comparing the different matrices it was observed that the fire risk was similar between the composites with unsaturated polyester and Modar matrices. However, the ignition time is longer for the modified than for the polyester matrix composites. The smoke hazard of fire was clearly lower for the Modar matrix composites due to the char forming property of this resin.

From TGA results it was observed that the Modar matrix composites were more resistant to temperature than the composites with polyester matrix due to the presence of acrylic acid as modifier. They showed also higher residual mass, which is another indication of char formation.

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