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THERMAL STABILITY AND MECHANICAL PROPERTIES OF SISAL IN CYCLE PROCESS

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In this study, the thermal stability of sisal in cycle process was investigated between room temperatures and 600°C in various conditions (in air, in composites, in argon) by thermogravimetry and mechanical testing measurement. The results indicated that the thermal stability of sisal was worse in air before five times of thermal cycles, but after the five times thermal stability of sisal in composites was better. In different conditions of same cycles process, the thermal stability of sisal was different. With increasing of thermal cycles times, the max. load (is the maximum strength in stress-strain curve) of sisal fiber showed downtendency in different conditions and decreased most obviously in composites.

Keywords: *cycle process, mechanical properties, sisal, thermal stability, thermogravimetric analysis*

Introduction

In the past decade, the growing environmental awareness has resulted in a renewed interest in the use of natural materials for different applications [1–4]. The new and harder environmental policies have forced industries like the automotive, packaging and construction industries to search for new materials that can substitute the traditional composite materials consisting of a plastic matrix and inorganic filler as reinforcement. The most used composites nowadays are the glass fiber filled thermoplastics, and different inorganic fillers like aramid or carbon fibers are widely used.

However, inorganic fibers present several disadvantages, i.e., their non-biodegradability, the abrasion that they produce in the processing equipment and the health problems that they cause to workers due to the skin irritations they produce during processing and handling. Sisal fiber is one of the most widely used natural fibers and is very easily cultivated. It has short renewal times and grows wild in the hedges of fields and railway tracks [5]. Nearly 4.5 million tons of sisal fibers are produced every year throughout the world. Tanzania and Brazil are the two main producing countries [5]. At present, sisal fiber is mainly used as ropes in the marine and agriculture industry [6, 7]. Other applications of sisal fibers include twines, cords, upholstery, padding and mat making, fishing nets, fancy articles such as purses, wall hangings, table mats, etc. A new potential application is for manufacture of corrugated roofing panels that are strong and cheap with good fire resistance [8].

In recent years, sisal-fiber-reinforced thermoplastics composites have gained much more interest among material scientists and engineers than thermosets, because of their low cost and recyclable properties. Many papers [9–12] have been published to explore the mechanical, environmental, electrical and dynamic properties of these composites rather than sisal-fiber-reinforced thermosets. In our previous article [13], complex building moulding board is prepared by recombination of sisal fibers and textile fabric with PVC regenerated plastic matrix. PVC regenerated plastic matrix was used in this study too. So our raw materials can decrease the growing environmental awareness.

It is known that thermoplastics are processed and used for many times, and sisal-fiber-reinforced thermoplastics are utilized for many cycles too. But when some materials are processed once or many times, their structures and properties (such as thermal properties, mechanical properties, etc.) will change to some degree. The purpose of this study is to investigate how the structures and properties of sisal fiber change after processing several times and how many times the sisal fiber can be used in thermoplastics composites.

Experimental

Materials

Sisal fibers and yarns were from Guangxi Sisal Company in Guangxi province, China. The average density of the fibers as 1.26±0.03 g cm^{-3} measured in a helium pycnometer with 10 runs for each one of the 10 samples analyzed [14]. And the average chemical composition for this variety is as follows: 75.2±0.3% cellulose, 13.9±0.1% hemicellulose, 8.0±0.1% lignin and 0.87±0.01% ash [15, 16].

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Waste PVC resin powder was obtained from Xi Long Plastic Company in Hubei province, China. Heat stabilizer of PVC, glycerol and argon were used.

Preparation of samples

Thermal treatment in air

Sisal fibers with a length of 50 to 100 mm were divided into four parts. The four parts of sisal fibers were taged A1, A5, A10 and A15. A1 fibers were roasted in an oven at 185°C for 30 min, A5 fibers were roasted in an oven at 185°C for 5·30 min too, A10 fibers were thermally treated in the same methods for 10·30 min and the final part of A15 fibers was processed for 15·30 min. All samples were cooled and airproofed in plastic bags.

Thermal treatment in composite

Four parts of sisal yarns with a length of 50 to 100 mm were prepared. The four parts of sisal fibers were taged B1, B5, B10 and B15. Some PVC regenerated sheets were obtained by waste PVC resin powder and heat stabilizer through calendaring and plasticizing of the missile plate. At 185°C and under 5 MPa press, two PVC regenerated sheets and B1 sisal yarns were laminated by hot-press for 30 min. Then sisal yarns were extracted from the composite and some sisal fibers ranging from 50 to 100 mm were obtained. In the same method, sisal yarns of B5, B10 and B15 were thermally treated for 5, 10 and 15 times (each time is 30 min) then the samples of thermal process in composites were obtained. Finally all samples were cooled and airproofed in plastic bags.

Thermal treatment in argon

Four parts of sisal yarns with a length of 50 to 100 mm were prepared. The four parts of sisal fibers were taged C1, C5, C10 and C15. All sisal yarns were placed in a flask full of argon and thermally processed in 185°C glycerol bath. And C1, C5, C10 and C15 yarns were thermally processed once, 5, 10 and 15 times (each time is 30 min) by above method. Then all samples of thermal process in argon were obtained. At last all samples were cooled and airproofed in plastic bags.

Methods

Thermogravimetric analysis

Thermogravimetric (TG) analyses were carried out using a thermogravimetric Analyzer (TG Q50, TA Instruments, New Castle, DE, USA). The specimens with 7.5 mg were placed in a ceramic crucible and heated from 20 to 650°C at 20°C min^{-1}, under nitrogen atmosphere (20 mL min^{-1}).

Mechanical properties testing

Tensile properties of sisal fibers were measured by using on Zwick 1465 Universal Testing Machine (UTM) at a crosshead speed of 40 mm min^{-1} and a gauge length of 30 mm. A standard UTM ultimate tensile strength at break was tested. Then max. load (is the maximum strength in stress-strain curve) was recorded. At least thirty specimens were determined for each sample and mean values were reported.

Results and discussion

The sample A0 is sisal fiber with not any treatment; A, B, C stand for sisal fibers by thermal cycles process in air, sisal fibers by thermal cycles process in composites, sisal fibers by thermal cycles process in argon, respectively. Numbers 1, 5, 10, 15 denote 1, 5, 10 and 15 times, respectively. These symbols apply throughout the next.

Thermogravimetric results

Thermogravimetric curves and thermogravimetric differential curves of raw sisal fiber (A0) in thermal process are shown in Fig. 1. The temperatures used for the analysis were from 30 to 600°C. For sisal fiber, dehydration as well as degradation of lignin occur in the temperature range from 60 to 200°C and most of the cellulose were decomposed at the temperature of 350°C. Generally speaking, in DTG curves the peak observed at 65°C for sisal fiber corresponds to the heat of evaporation of water from the fiber (stage 1). The second peak of sisal at about 350°C is due to the thermal depolymerisation of hemicellulose and the cleavage of the glycosidic linkage of cellulose (stage 2). The third peak (at about 550°C) for sisal fiber may be due to the further breakage of decomposition products of stage 2, leading to the information of tar [17]. But in

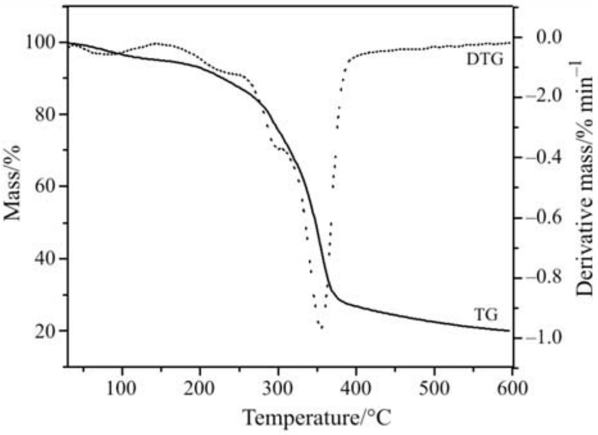

Fig. 1 TG /DTG curves of raw sisal

our thermogravimetric differential curves, the third peak is not obvious, as fiber decomposition is a very complicated process which is affected by the conditions of the reaction, e.g. calefative rate.

Effect of cycle times on thermal stability

Figure 2 reveals that before 5 times the second peak moved to the left, i.e., the decomposition temperature of stage 2 was little lower. But the second peak moved to the right from Fig. 4. In the composites, the decomposition temperature of stage 2 did not change before 5 times. In stage 2, the thermal depolymerisation of hemicellulose and the cleavage of the glycosidic linkage of cellulose were decomposed. Probably, before the 5 times, at 185°C, pectin and some impurity were decomposed slowly and the decomposition temperature was affected by content of oxygen.

But after 5 times of thermal cycles, the decomposition temperature increased obviously, as shown in Fig. 3. After 5 times of thermal cycles in composites, the components at lower temperature were decomposed completely, so the other components were decomposed later before 5 times. And, before 5 times of thermal treatment, some fibers were oxidated and crystallinity stucture of sisal fibers was breaken, but after 5 times, the crystallinity degree increased due to the change of crystallinity structure affected by the resin of the composites, so the second peak of decomposition moved to the higher temperature. In Figs 2 and 4, the change is not obvious.

These indicate that sisal fibers are used cycles, with the times increasing, the thermal stability changed gradually. Before the 5 times, the thermal stability changed unobviously except in air, but over 5 times, the thermal degradation of sisal fiber will become good in the composites. That is to say, when the sisal reinfores composite, the thermal stability of fiber is good after cycled use. But over some times, the properties of materials is too worse to satisfy the conditions of use, because there are various factors influencing the properties.

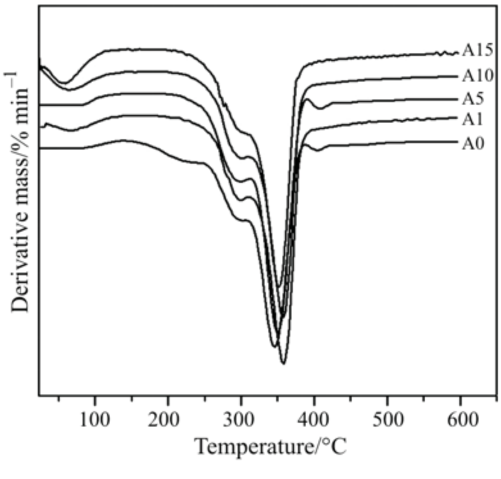

Fig. 2 DTG curves of sisal fibers by thermal cycle times in air

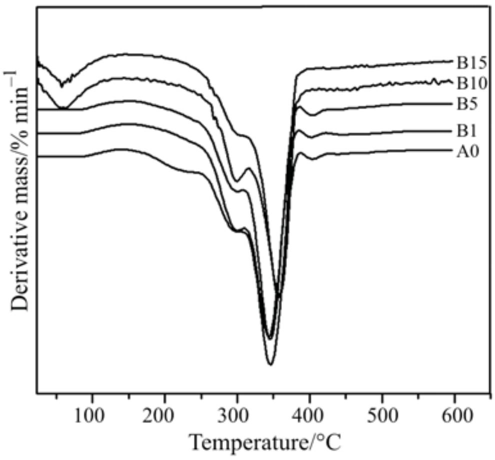

Fig. 3 DTG curves of sisal fibers by thermal cycle times in composites

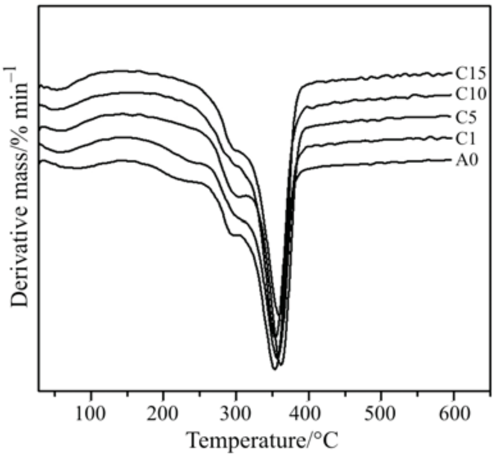

Fig. 4 DTG curves of sisal fibers by thermal cycle times in argon

Effect of different conditions on thermal stability

Sisal fibers were thermally treated in three different levels of atmosphere (in air, in composite and in argon). Their TG curves in the same cycle times are presented in Fig. 5I–IV. Figure 5I indicates that before 203°C, C1>A1>B1 in the same temperature, between 203 and 373°C, the order of mass loss in the same temperature was C1>B1>A1, and after 373°C the order of mass loss in the same temperature is C1>A1>B1. Figure 5II present the same trend as Fig. 5I. These are similar to three decomposed stages. The different results can be explained by the fact that in argon is more propitious to the evaporation of wa-

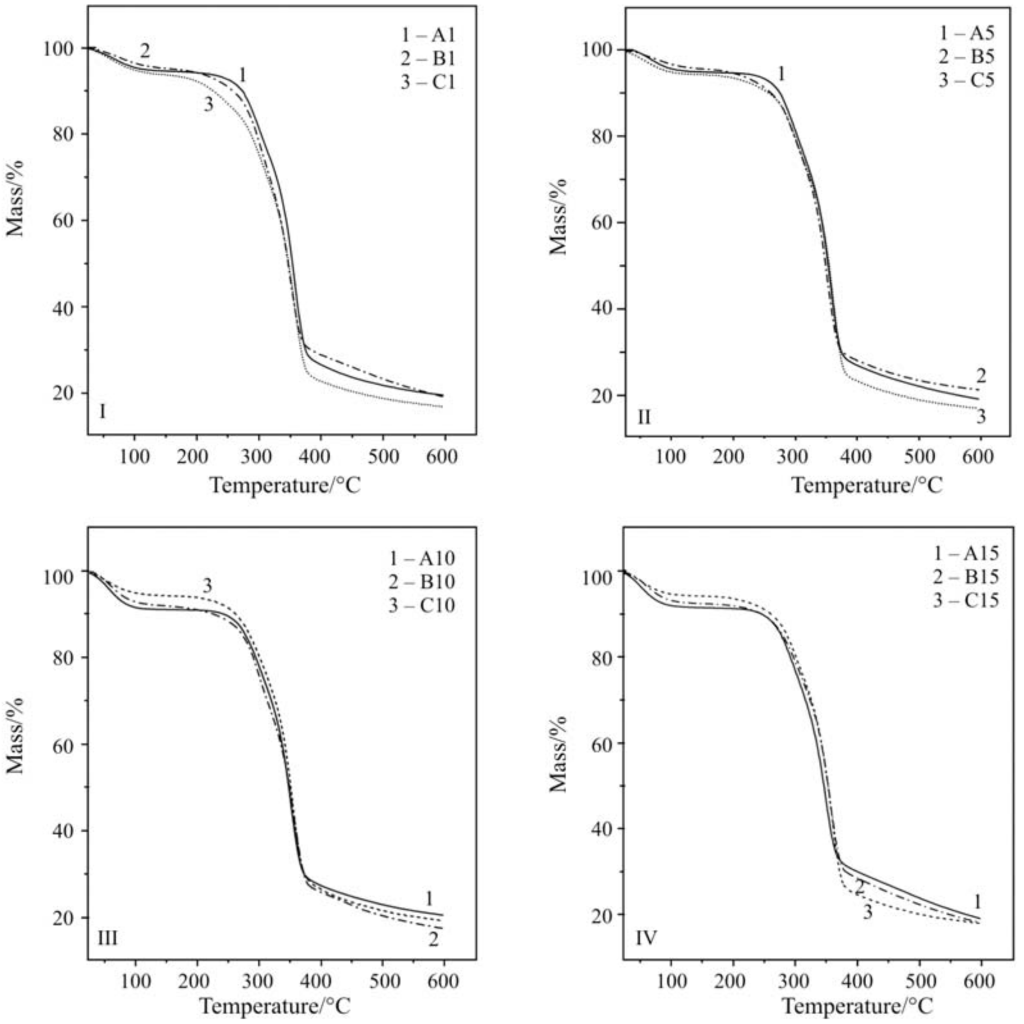

Fig. 5 TG curves of sisal fibers in different atmosphere with same cycle times; I – 1, II – 5, III – 10 and IV – 15 times

ter and small molecular than in air and in composites, and the decomposition of the second stage in composite is quicker than those in air and in argon, because of the effect of the resin decomposition in composites.

Figures 5III and IV show that before 210°C the order of mass loss in same temperature was A10>B10>C10 and A15>B15>C15. It is explained by the fact that after times of thermal treatment, water and small molecular have been evaporated mainly, pectin and some impurity were decomposed slowly, and the decomposition temperature was affected by content of oxygen. So before 210°C, sisal fibers were decomposed severely in more content of oxygen. Between 210 and 372°C, about thermal stability of sisal fibers in different conditions by 10 or 15 times of cycle process, the difference was not obvious. After 373°C, Figs 5III and IV show that the order of mass loss in same temperature was B10>C10>A10 and C15>B15>A15. In this instance, the content of oxygen is not main effective factor. The thermal depolymerisation of hemicellulose and the cleavage of the glycosidic linkage of cellulose (stage 2) produced some new small molecular. Over 10 times of thermal cycle process, the PVC resin was ageing severely and some dissociative molecule brought, which may induce the decomposition of matter (in stage 3). Because after more times of thermal cycle process, crystallinity of sisal fiber heightened. Yang Guicheng *et al*. [18] reported crystallinity of sisal fiber increased by thermal treatment at 180°C. And in no oxygen, crystal lattice of sisal was more integrated than other conditions after more times of thermal cycle process. So the order of mass loss after 373°C was C15>B15>A15.

Effect of thermal cycle process on mechanical properties

Max. load (is the maximum strength in stress-strain curve) of sisal fibers with cycles process in different conditions are shown in Table 1. It reveals that the tensile strength decreased with the increase of times

Table 1 Max. load of sisal fibers by thermal cycles

	Sample												
	A0 raw sisal fiber	A sisal fiber by thermal cycles process in oxygen				B sisal fiber by thermal cycles process in composites				C sisal fiber by thermal cycles process in no oxygen			
Cycle times	0	1	5	10	15	1	5	10	15	1	5	10	15
Max. load/N	10.94±0.58	6.18±0.36	2.57±0.42	1.68±0.27	1.11±0.21	6.63±0.45	1.03±0.19	–	–	8.21±0.55	4.45±0.41	2.01±0.34	2.21±0.36

The length of sisal fibers do not reach to testing length by thermal cycles(10 and 15 times) in composites,so the data of B10 and B15 do not obtain.

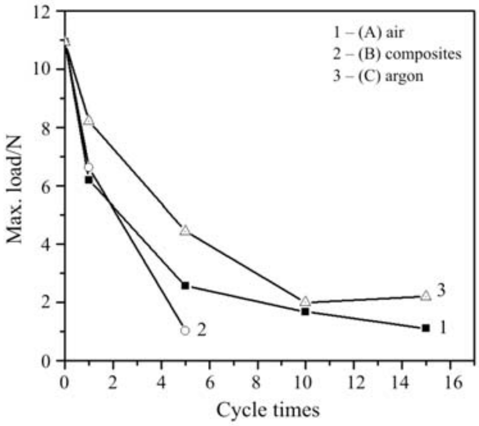

Fig. 6 Curves of max. load of sisal fibers by thermal cycles

of thermal cycles gradually, as can be seen in Fig. 6. In addition max. load by thermal treatment in air declined greater than in argon (curve A *vs*. curve C) and in the composites the max. load of sisal fibers declined obviously.

Different researchers [19–21] reported that the mechanical properties of sisal fibers effected by fiber itself such as structure, age and experimental conditions such as fiber length, test speed, etc. In the process of thermal treatment, due to some components of fiber decomposing, with the increase of times of thermal cycles the molecular mass declines gradually and in the fiber surface the inanition and disfigurement are formed, so max. load of sisal fiber shows degressive trend. Because in air sisal fibers are oxidated in the thermal treatment, the max. load of sisal fiber in air is worse than in argon. Although sisal fibers are under anoxic condition in composites, the effects of the resin and the pressure of moulding led to the lowest max. load in composites.

When the life of materials is over, we must stop using them. Because if you use them again, a bad effect will occur. For example, when sisal fibers were used to reinforce composites, its properties did not meet our needs, in the composites, it is disfigurement and bad ingredient.

Conclusions

We present original experimental results of the thermal stability of sisal in cycle process. It appears that the thermal degradation of sisal is 3 stages. The results indicate that the thermal stability of sisal was worse in air before 5 times of thermal cycles, since at 185°C, pectin and some impurities were decomposed slowly and the decomposition temperature was affected by content of oxygen, but after 5 times the thermal stability of sisal in composites was better, because the crystallinity degree increased due to the change of crystallinity structure affected by the resin of the composites, so the second peak of decomposition moved to the higher temperature. In other conditions, the thermal stability of sisal changed unobviously. In different conditions of same cycle process, the thermal stability of sisal was different. Before 5 times, the order of mass loss of sisal in the same temperature was C>A>B before 203°C or after 373°C and is C>B>A between 203 and 373°C. At 10 and 15 times of thermal process, the results were A>B>C before 210°C, B10>C10>A10, C15>B15>A15 after 373°C and no obvious difference between 210 and 373°C. The content of oxygen, resin and increase of crystallinity were the effective factors. With increasing of thermal cycles times, the max. load showed downtendency in different way, and it decreased obviously in composites. Although the thermal stability of sisal in composites became better, the effective factors of materials are various, e.g., mechanical properties, crystallization and so on. Therefore the useful life span of sisal in cycle process is limited.

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