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Carboxylation Modification of Fiber Reclaimed from Old Newspapers and Its Effects on Properties of the Reinforced Polylactic Acids Composites

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Abstract. In order to make full use of old newspapers and preserve precious plant resource, old newspapers were reclaimed and refined into fiber, then phthalic anhydride(PA) was utilized to modify the reclaimed-fiber on the condition of ultrasonic radiation. Subsequently, reclaimed-fiber was mixed with polylactic acids(PLA) to obtain composites by means of extrusion molding. At last, mechanical performances of the composite were tested. Results reveal that: composite made form PLA and the PA treated reclaimed-fiber from old newspapers has good mechanical performances, and its tensile strength is higher than 41.5MPa while impact strength is no less than 7.3KJ/m^2. Moreover, the optimum processing conditions for modifying reclaimed-fiber with PA are: mass fraction of phthalic anhydride to old newspaper reclaimed fiber 5%, ultrasonic radiation time 15min, and modification temperature 90℃.

Introduction

Newspaper, as a reproducible resource made form plant fiber, can be reasonably utilized even after it has finished serving its informing and enlightening function. When old newspapers were processed by means of pulp beating, drying and so on, reclaimed plant fiber with high specific strength and specific modulus can be obtained, which is able to act as reinforcing agent in the polymer composites[1-2].

In 1990's, Mitsubishi Corporation of Japan has manufactured the auto parts with composite materials of waste paper recycled fiber and polypropylene. References also reveal that the biologically degradable plastic composite material prepared from waste paper recycled fiber and polylactic acids can be used as the auto interior decoration parts, household appliances shell and so on. As an innovative way of recycling the waste newspapers, obtaining fiber from old papers by means of beating and refining does have its disadvantages since the reclaimed fiber has much polar groups like hydroxyl. These polar groups have strong chemical polarity while the plastic has the non-polar surface, so their compatibility is not desirable, leading to a weak bonding power and a negative effects on the physical and mechanical performance of the composite[3-4]. Consequently, treating the plant fiber with modifier so as to reduce its surface polarity is an acceptable method to increase the compatibility of plant fiber and the degradable plastic [5]. At present, maleic anhydride grafted polypropylene, silane coupling agent and titanate coupling agent are mostly used to treat the plant fiber and the modification effects are acceptable[6]. In this paper, in order to widen the methods of modifying plant fiber, the fiber recycled from old newspaper was treated with PA on the condition of ultrasonic radiation and the effects of PA on the modification was investigated.

Materials and Methods

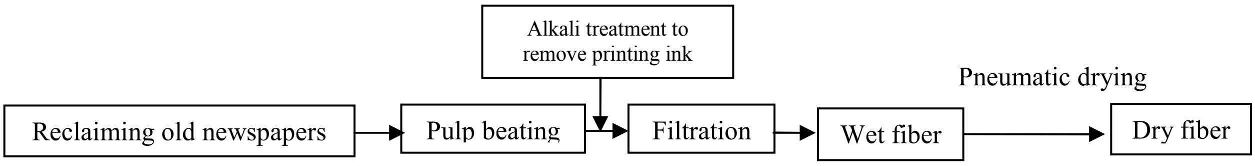
Experiment materials. Old newspaper. Polylactic acids, ESUNMP1001 granular, Shenzheng Guanghuaweiye Corporation. Phthalic anhydride and ethanol, analytically pure, Jiangyin Zhongrun Chemical Corporation. Self-made fiber reclaimed from old newspaper(the manufacture process see picture 1). Sodium hydroxide, analytically pure, Hunan Huihong Reagent Limited Corporation.

Testing instruments. 1510 ultrasonic cleaning tank, Taizhou Taiyu Electronic Limited Corporation. 101A-3 electronic thermostatic drying chamber, Shanghai experiment instruments plant. JY digital balance, Shanghai Puchun Metrical Instruments Corporation. XK160 rubber refiner, Qingdao Huashenglong Rubber Machinery Limited Corporation. JPH80G injection molding machine, Guangdong Xiongzheng Plastic Machinery Limited Corporation. DCS-R-100 mechanics machine, Japan Shimadzu Corporation.

Testing methods.

Modification of reclaimed-fiber. Fiber reclaimed from old newspaper old newspapers were dried before suspended in ethanol (mass ration of fiber to ethanol 1:10), subsequently, the suspension was put in the ultrasonic washing tank to be pre-treated. PA was added to the pre-treated suspension under stirring conditions, then the whole system was placed in the oil bath at certain temperature to react for some time. After this, the reaction products were cooled to atmospheric temperature, filtered, washed and dried in the drying oven at the temperature of 70℃ for 12h.

In the process above, treatment conditions of modifying the fiber follow the orthogonal test table, in which phthalic anhydride amount, modification temperature and time of ultrasonic treatment are factors. Orthogonal test schemes see table1.



Picture 1 Process flow of reclaiming fiber from old newspaper

Table 1 Orthogonal test table

Levels	Factors		
	A PA amount (%)	B ultrasonic treatment time (min)	C ultrasonic treatment temperature (℃)
1	4	10	90
2	5	15	100
3	6	20	110

Notes: PA amount is PA's mass fraction to reclaimed-fiber

Preparation of composites. Dried PLA and the modified reclaimed-fiber was sent to rubber mixing machine(mass ratio of PLA to fiber was 60: 40) and mixed for 10 min at the temperature of 170°C to obtain schistic compound. Subsequently schistic compounds was poured to the plastic shredder to be crashed into granule products, which were later put to the injection molding machine to get the standard testing samples. The technological parameter of injection molding were as follows: three feed cylinder temperature were sequentially 160°C, 170°C and 180°C; injection pressure was 13MPa and pressure maintaining time was 15s.

Mechanical performance tests of the composites. Tensile strength and impact strength The composite testing sample were respectively tested on the mechanical testing machine and impact strength testing machine to get the corresponding tensile strength value and impact strength value. Tensile strength tests were conducted according to GB/T1040.1—2006 and impact strength tests GB/T13525—92.

Results and discussions.

Test results see table 2 and table 3. At first, test results were calculated and analyzed according to the single index, then all the single index results were comprehensively balanced to determine the optimum modification treatment. The K, k, R of each factor were calculated according to the tensile strength and impact strength, thereafter, the pictures of k plotted to factors and levels were drawn.(see picture 2 and picture 3).

It can be seen from table2, table3, picture2 and picture3 that the important order of relevant factors that affect tensile strength and impact strength is: treatment temperature(C) > PA amount (A) >ultrasonic treatment time(B). That is to say, modification temperature exerts most influence on strength. The reasons for this are as follows: when modifier phthalic anhydride is added to ethanol suspension of fiber, hydrogen ions of the former react with the hydroxyl on the C_2 and C_3 position of cellulose of fiber, therefore, polarity of fiber is reduced. Seen from the test results is that: at first, with the increase of PA amount, the reaction positions---sites around the hydroxyl—can supply more anhydride, leading to the greater possibility of hydroxyl's collision into the anhydride. In this way, carboxylation reactions are easier to occur and modification effects are more manifest, rending the mechanical performance of composites better. Anyway, with the increase of PA amount, i.e., increased to more than 5%, the excessive PA reduces the mechanical performance to some extent. In conclusion, the optimum mass fraction of PA to the reclaimed fiber is 5%.

Table 2 Tensile strength results of the orthogonal test

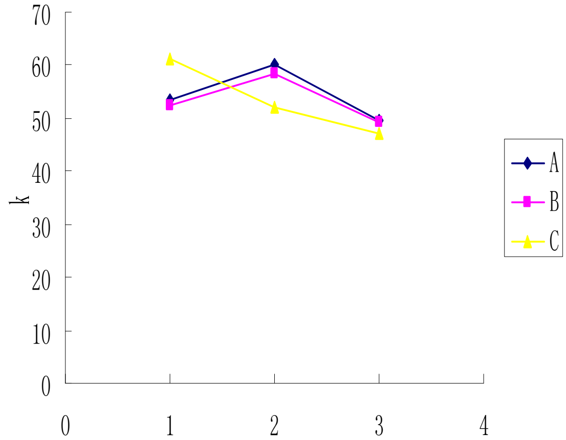
Test number	A	B	C	Tensile strength (Mpa)
1	1	1	1	55.6
2	1	2	2	53.4
3	1	3	3	42.7
4	2	1	2	60.3
5	2	2	3	56.8
6	2	3	1	63.2
7	3	1	3	41.5
8	3	2	1	64.8
9	3	3	2	42.2
K1	160.7	157	183.6	
K2	180.3	175	155.9	
K3	148.5	148	141.0	
k1	53.6	52.5	61.2	
k2	60.1	58.3	51.9	
k3	49.5	49.4	47.0	
R	10.6	8.9	14.2	

Table 3 Impact strength results of the orthogonal test

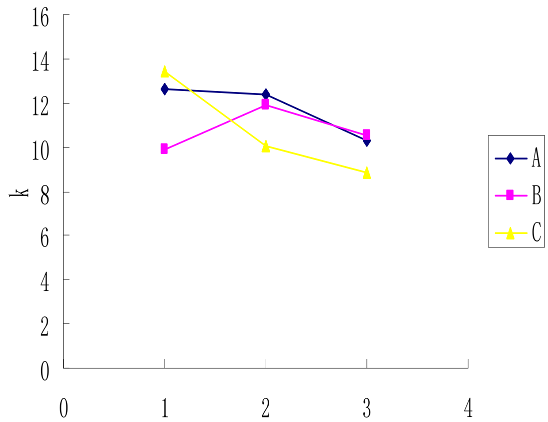
Test number	A	B	C	Impact Strength (KJ/m2)
1	1	1	1	10.5
2	1	2	2	9.8
3	1	3	3	8.6
4	2	1	2	11.9
5	2	2	3	10.7
6	2	3	1	14.5
7	3	1	3	7.3
8	3	2	1	15.2
9	3	3	2	8.4
K1	37.9	29.7	40.2	
K2	37.1	35.7	30.1	
K3	30.9	31.5	26.6	
k1	12.6	9.9	13.4	
k2	12.4	11.9	10.3	
k3	10.3	10.5	8.9	
R	2.3	2.0	4.5	

As for the ultrasonic treatment temperature, temperature can improve the motion energy of molecules, which is able to promote the diffusion of ethanol into the interior of fiber and intensify its swelling. With this, possibility of the modifier's collision with hydroxyl is increased so does the modification effects. Nevertheless, test results show that too high a temperature is detrimental to the reaction since the mechanical performances are reduced. The reasons maybe too high a temperature can bring about the degradation of modification products on the given condition in these experiments. Test results show that the appropriate reaction temperature is less than or equal to 90℃.

For ultrasonic pre- treatment time, proper time is beneficial to the reaction of reclaimed fiber and PA for reasons that when ethanol suspensions of fiber are exposed to the ultrasonic, its mechanical effects can produce intense jet flow and partial mircro-swashing in the suspension, both of which promotes the swelling of reclaimed fiber. Meanwhile, ultrasonic treatment can cause deformation in the defect positions on the surface of fiber even the formation of micro holes, rending the surface area of fiber increase, which benefits the modification reaction[6]. However, further prolonged ultrasonic pre- treatment time can exert negative effects on the modification, it is because too long a ultrasonic mechanical treatment time reduces the strength of fiber, leading to an inferior mechanical properties of composites. Consequently, on the given condition in these experiments, appropriate ultrasonic pre-treatment time is less than or equal to 15min.



Picture 2 Effects of factors and levels on the tensile strength indicates



Picture 3 Effects of factors and levels on the impact strength indicates

Conclusions

PA was used to modify the fiber reclaimed from old newspaper under the condition of ultrasonic radiation and the treated fiber was mixed with PLA to get the composites, whose mechanical properties were tested later. Following conclusions can be drawn:

(1) Phthalic anhydride, used as modifier to treat old newspaper reclaimed fiber, can enhance the mechanical performances of the reclaimed fiber reinforced polylactic acids composites, as the tensile strength is higher than 41.5MPa and impact strength no less than 7.3KJ/m^2

(2) During the modification treatment, temperature exerts the premier effects on the modification effects and PA amount and ultrasonic pretreatment time sequentially follows. The optimum processing condition is mass fraction of phthalic anhydride to reclaimed-fiber 5%, modification temperature 90 ℃ and processing time 15min.

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