Preparation and Process Optimization of Eucommia Gutta percha Based Shape Memory Materials

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Abstract: The sulfur system of conventional unsaturated rubber can be used to vulcanize and cross-link Eucommia ulmoides gum (EUG) moderately and destroy its partial crystallization. By adjusting the ratio of crystallinity and cross-linking degree, EUG can be made into thermotropic shape memory materials which respond to different temperatures, and the optimal formula was selected by orthogonal design. The EUG-based shape memory materials were prepared with this formula have a thermal stimulation memory execution temperature close to the normal body temperature and good shape recovery capability, which will be expected to be used as a pressure-sensitive adhesive material for transdermal drug delivery systems (TDDS) under human physiological conditions.

Keywords: *eucommia ulmoides gum; shape memory material; process optimization*

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Introduction

Thermotropic shape memory polymer material is a kind of functional materials that can respond to temperature changes and adjust itself to deform, which has a two-phase structure, namely a stationary phase and a reversible phase [1]. When it is heated to a certain temperature, an external force is applied to deform it, and it is cooled rapidly in the deformed state to freeze the stress; When it is heated above a certain temperature again, the stress of the material will be released, which will make the material automatically return to its original state. EUG is a kind of natural rubber derived from the leaves, fruits, barks and roots of Eucommia ulmoides Oliver, and its yield is abundant. Although it has the same chemical composition $(C_5H_8)_n$ as ordinary natural rubber, it is trans-polyisoprene structure, which has unique "rubber-plastic duality" [2], and has plasticity and high elasticity, and its melting point is about 60℃. It has been successfully applied to medical gypsum substitute, medical orthopedic material, drug sustained-release material [3].

2 Experimental Methods

2.1 Materials

EUG (＞94%) was purchased from Lueyang Jiamu Eucommia ulmoides industry Co., Ltd., Shaanxi Province, China. Zinc carbonate and talc were purchased from Tianjin Recovery Fine Chemical Research Institute, Tianjin, China. Sulfur and titanium dioxide were purchased from Zhejiang Yinuo Biotechnology Co., Ltd., Zhejiang Province, China. Zinc diethyldithiocarbamate (ZDC) and N-cyclohexylbenzothiazole-2-sulphenamide (CZ) were purchased from Wuhan Lanabai Medicine Chemical Co., Ltd., Hubei Province, China.

2.2 Formula

Basic formula: 1g gutta percha; Talcum powder 0.15g; 0.02 g zinc carbonate; 0.005g accelerator; 0.02 g sulfur; Titanium dioxide 0.15g.

2.3 Preparation process

Mixing process: at about 80 ℃, add EUG and mix for about 5min. After the rubber material is completely softened, add talcum powder, antioxidant (titanium dioxide), accelerator (CZ, ZDC), zinc carbonate and other auxiliary materials in turn, then add sulfur. After mixing, vulcanize at 150 ℃ for 30min [4].

2.4 Measurement of shape recovery rate of the materials

After marking a marking line with a pitch of L_0 on the sample, which was fixed between stretching jigs, raised the temperature to 60 ℃ in a uniform temperature field, kept the temperature constant for 5 min, and then the sample was stretched along the direction of gauge distance by L_a, kept the external stretching force to cool quickly at room temperature, and then the deformation was fixed, removed the external force, measured the distance L_b between the two marking lines, and put into a uniform temperature field with the temperature of 60 ℃. At this time, the measured distance between the two lines was Lc, and the shape recovery rate (R_r) was calculated using [5-6]:

$$R_r = (L_c-L_0)/(L_b-L_0) \times 100\% \quad (1)$$

2.5 Measurement of thermal stimulation memory execution temperature of the materials

The sample was cut into small strips with a length of

30 cm and a width of 5 mm, and stretched to the maximum yield length in a water bath at about 70 ℃, and then the sample was quickly cooled while maintaining the external force, and the deformation was fixed, put into a room temperature water bath, hanged 1 g weight, and a heating rate of 1 ℃/min. The retraction temperature of the sample was observed, which was measured three times for each sample, and the average value was the thermal stimulation memory execution temperature of the sample.

3 Results and Discussion

3.1 Single factor experiment results and analysis

3.1.1 Effect of sulfur consumption on execution temperature of thermal stimulation memory of materials

Sulfur is added to the gutta percha to make linear gutta percha molecules cross-linked to form a network structure under heating, thus increasing the strength of gutta percha and improving its elasticity and solvent resistance [7]. It can be seen from the above experimental results that, with the increase of sulfur consumption, the proportion of - S-S-bond in the chain structure directly increases, making its cross-linking density increase, hindering the movement of the molecular chain segment and the crystallization ability. At the same time, the proportion of the amorphous region also increases significantly, leading to the decrease of crystallinity and the decrease of its thermal stimulation execution temperature (as shown in Figure 1a).

3.1.2 Effect of accelerator ratio on the execution temperature of thermal stimulation memory of materials

In order to ensure the safety of the operation in the curing stage and the scorching property of the rubber compound, and take into account the safety, non-toxic, melting point and other physical properties of the reagents used, CZ and zinc diethyldithiocarbamate (ZDC) are selected as the mixed accelerator. It can be seen from the above experimental results that when the amount of sulfur is constant and the total amount of accelerant is constant, the execution temperature of thermal stimulation memory of the material first increases and then decreases (as shown in Figure 1b) with the increase of the ratio of accelerant ZDC to CZ. When the ratio of accelerant is between 4:1-5:1, the execution temperature of thermal stimulation memory of the material is between 36-37 ℃, close to the normal body temperature, with good effect.

3.1.3 Effect of the amount of zinc carbonate on the execution temperature of thermal stimulation memory

In order to improve its shape stability and remove H2S gas generated during vulcanization, we added a certain amount of zinc carbonate, which can improve the thermal conductivity and vulcanization speed of the rubber compound. However, with the increase of the amount of zinc carbonate, the thermal stimulation memory execution temperature of the material does not change significantly (as shown in Figure 1c), which may be related to that zinc carbonate can increase the thermal conductivity of the compound and improve its thermal conductivity.

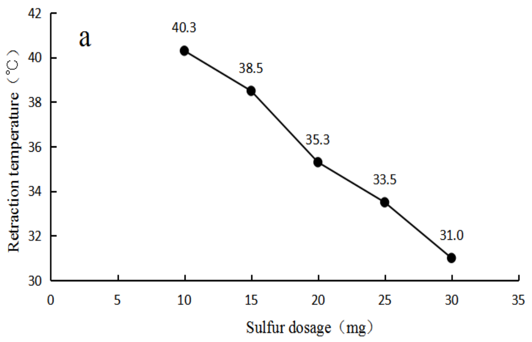
3.1.4 Effect of titanium dioxide dosage on the execution temperature of thermal stimulation memory

At the same time, we added titanium dioxide to improve the appearance of EUG based shape memory materials and prevent their oxidation. With the increase of the amount of titanium dioxide, the execution temperature of the thermal stimulation memory of the material increases slightly (as shown in Figure 1d).

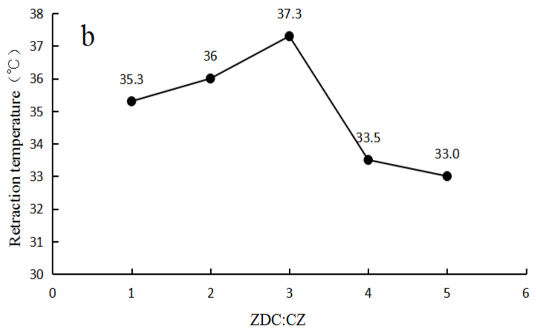
According to the above experimental results, with the increase of the amount of titanium dioxide, the thermal stimulation memory execution temperature of the material increases slightly, but the reason why it affects the thermal stimulation execution temperature of TPI is unclear. It may be that its addition acts as a nucleating agent and promotes the formation of crystals, thereby increasing the thermal stimulation temperature of TPI shape memory materials [8].

3.1.5 Effect of talc dosage on the execution temperature of thermal stimulation memory

Of course, in order to ensure the complete vulcanization of EUG, we added talcum powder as the reinforcing filler. On the one hand, it reduces the crystallinity and mechanical strength of EUG, facilitating the mixing of unvulcanized rubber; On the other hand, it plays a reinforcing role in the rubber compound, improving its constant elongation strength and tensile strength. It is precisely because of these two aspects that the change of talcum powder dosage has no significant effect on the execution temperature of thermal stimulated memory of materials (as shown in Figure 1e).



1-a



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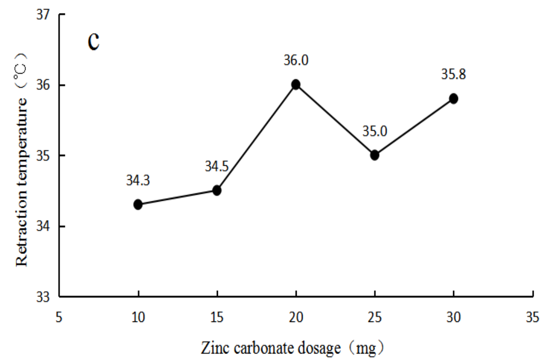

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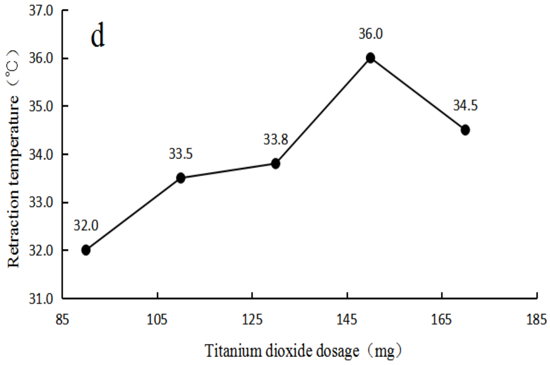

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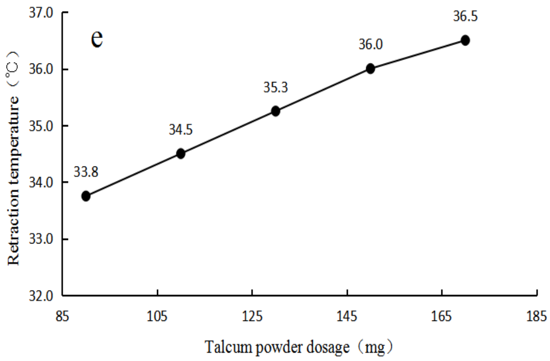

1-e

Figure 1 The effect single factor on the thermal stimulation memory execution temperature of the materials

3.2 Orthogonal experimental design and result analysis

On the basis of pre-test and single factor investigation, the prescription was optimized through orthogonal test design. The dosage of titanium dioxide and talcum powder was 150mg. Three factors and three levels orthogonal test were designed with the dosage of sulfur (A), accelerator ratio (B) and zinc carbonate (C) as three factors, The performance temperature of thermal stimulation memory of materials and the shape recovery rate of materials were used as evaluation indicators to screen the prescription process. The main factors and their levels were shown in Table 1, and the test results were shown in Table 2.

Table 1 Factors and levels

Levels	Factors		
	A Sulfur dosage (mg)	B Accelerator ratio	C Zinc carbonate dosage (mg)
1	18	4:1	15
2	20	5:1	20
3	22	6:1	25

Table 2 Orthogonal design test table for prescription screening of thermotropic shape memory polymer materials

Batch		Factors			Response rate (%)	Retraction temperature (℃)
		A	B	C		
1		1	1	1	97.1	35.0
2		1	2	2	96.8	37.0
3		1	3	3	97.2	36.0
4		2	1	2	96.9	35.5
5		2	2	3	97.6	35.0
6		2	3	1	95.9	36.5
7		3	1	3	96.1	33.0
8		3	2	1	93.6	32.5
9		3	3	2	96.3	32.0
Response rate	K_1	97.03	96.70	95.53		
	K_2	96.80	96.00	96.67		
	K_3	95.33	96.47	96.97		
	R	1.70%	0.23%	1.44%		
Retraction temperature	K_1	36.00	34.50	34.67		
	K_2	35.67	34.83	34.83		
	K_3	32.50	34.83	34.67		
	R	3.50%	0.50%	0.17%		

For the shape memory polymer materials, the higher shape recovery rate was, the stronger its ability to keep shape would be, and the more beneficial it was to its application. Therefore, according to the analysis of orthogonal experimental results (Table 2), the best experimental scheme of combining the optimal levels of various factors was $A_1B_1C_3$.

As this material will be applied to human body as TDDS pressure sensitive adhesive material, the thermal stimulation memory execution temperature of the material should be close to the normal body temperature. And consequently, It could be seen from Table 2 that the best experimental scheme of combining the optimal levels of all factors was $A_1B_2C_2$ or $A_1B_3C_2$.

3.3 Determination of final experimental scheme

According to the orthogonal experimental optimization schemes $A_1B_1C_3$, $A_1B_2C_2$ and $A_1B_3C_2$, three batches of samples were prepared for each scheme, and the thermal stimulation memory execution temperature and the shape recovery rate of the three batches of samples were measured respectively. The results were shown in Table 3.

Table 3 The results of thermal stimulation memory execution temperature and shape recovery rate of each batch of sample in each scheme

Samples	Retraction temperature (℃)			Response rate (%)		
	1	2	3	1	2	3
$A_1B_1C_3$	35.0	35.5	35.0	95.2	95.8	97.4
RSD (%)		0.83			1.18	
$A_1B_2C_2$	36.5	36.5	37.0	95.7	97.1	98.1
RSD (%)		0.79			1.24	
$A_1B_3C_2$	35.5	36.0	36.5	96.4	97.5	97.2
RSD (%)		1.39			0.59	

According to the above experimental results, the thermal stimulation memory execution temperature of the three batches of samples were prepared according to the prescription $A_1B_2C_2$ was closest to the normal body temperature, and the mean value of shape recovery rate was 97.0%, and the variance was less than 2%, which indicated the experiment reappeared well.

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4 Conclusion

The technological formula optimized by orthogonal design was composed of sulfur 18 mg, accelerator ratio 5:1 (ZDC 4.17 mg, CZ 0.83 mg), zinc carbonate 20 mg, titanium dioxide 150 mg and talc 150 mg. The thermal stimulation memory execution temperature of the sample prepared with the optimal formula was about 37℃, and the shape recovery rate of the material was good, which improved the performance of EUG. Overall, the research on the preparation and process optimization of Eucommia ulmoides gum-based shape memory materials laid a foundation for further using it as pressure sensitive adhesive material for TDDS. However, the feasibility and safety of the materials should be further studied.

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