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Thermal Stability of Short Sisal Fibre Reinforced ENR/PVC Composite

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The thermal degradation reactions of short sisal fibre reinforced ENR/PVC composite were analysed and studied. It was found that HCl was strongly generated from PVC in the composite between 266°C ~ 282.3°C, which resulted in an exothermal catalysed reaction of the ENR and accelerated the oxidative degradation of ENR/PVC blend. The addition of short sisal fibre raised the thermal stability of the composite. The thermal stability of the composite rose with the increasing amount of short sisal fibre and fell with the increasing ratio of PVC in the composite.

Key words: ENR; PVC; sisal fibre; composites; thermoanalysis; blend; thermal stability; short fibre

Epoxidised Natural Rubber (ENR) is a polar material prepared by the introduction of epoxy-group into natural rubber (NR) after modification. ENR is well compatible with PVC. Blending ENR with PVC to produce elastomer has been reported[1,2]. The natural rubber composite reinforced by short sisal fibre shows an obviously improved modulus and has such properties as high-strength, high-rigidity and swelling, and aging-resistance. This composite has been widely used in some specific conditions[3]. Sisal fibre is a kind of natural fibre composed mainly of cellulose. The sisal fibre adheres well to NR after acetylation[4]. The NR composite reinforced by short sisal fibre shows excellent physical properties[5]. In recent years, the ENR/PVC composite reinforced by short sisal fibre has been studied extensively by Liu and Zhang and an elastomer with increased hardness, high longitudinal tensile strength, very low elongation at break, low permanent set at break and good oil and aging resistance was obtained[6]. This elastomer has promising prospects in manufacturing oil-resistant seals. The thermal stability of short sisal fibre-ENR/ PVC composite has great influence on its application properties. The studies on thermal stability of this composite have its practical value. In this study, thermogravimetry/ derivative thermogravimetry (TG/DTG) and differential thermal analysis (DTA) methods were used to study the thermal stability of short sisal fibre-ENR/PVC composite.

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EXPERIMENT

Materials

ENR-50 was prepared by South China Tropical Agricultural Product Processing Research Institute. PVC (s-1000) was supplied by *QILU* petrochemical company. Sisal fibre was obtained from Sisal Product Quality-inspecting Center of the Ministry of Agriculture. Other materials were purchased from the market.

The ingredients used are shown in the formulation for ENR and PVC masterbatch (*Table 1*).

TABLE 1. FORMULATION FOR ENR AND PVC MASTERBATCH

Material	ENR Masterbatch (p.h.r.)	PVC Masterbatch (p.h.r.)
ENR-50	100	–
Sodium carbonate	6	–
Stabiliser	6	–
PVC	0	100
Stabiliser	–	5
DOP	–	40

The ENR and PVC masterbatches were blended together to obtain the ENR/PVC blend and the compounds are given in *Table 2.*

TABLE 2. FORMULATION FOR ENR/PVC BLENDS

Compound	(p.h.r.)
ENR/PVC	100[a]
ZnO	5
Stearic acid	2
TBBS (N-tert-Butyl-2-benzothiazolphenamide)	2
N-Phenyl-β-naphthylylamine	1
CTP [N-(cyclohexylthio) phthlimide]	0.5
Aromatic oil	10
HAF	30
Sulphur	1
Short sisal fibre[b]	100

[a]Variable ratio (90:10; 80:20; 70:30; and 60:40)
[b]Amount of resorcinol (1, 3-benzenediol) and hexamethylene tetramine are 25 p.h.r. and 16 p.h.r. respectively, in 100 p.h.r. of short sisal for RH bonding system
[c]Variable amount: 0, 20, 30 and 40 p.h.r.

Sample Preparation

The sisal fibres were cut into short lengths of about 10 mm long and acelylated by the methods stated by Varghere *et al.*[4], then washed and dried. The ENR masterbatch was prepared in a Φ160 mm mill.

The Φ160 mm high-temperature mill (roll temperature about 170°C) was used to plasticise the prepared PVC masterbatch. Then the ENR masterbatch was added in the mill and blended with the PVC masterbatch.

The ingredients and the short sisal fibre were added to ENR/PVC blend according to the usual compounding operation on the Φ160 mm mill.

The ENR/PVC composite reinforced with short sisal fibre was vulcanised in a 0.5 MN and 400 mm × 400 mm computer-controlled vulcanising press for preparing the test-pieces. The vulcanising condition was 143°C for 15 min.

Methods

A TG-DTA 320-thermal analyser made by Seiko company in Japan was used for thermal analysis. TG/DTG and DTA were carried out simultaneously. The temperature rise rate was 10°C min^{-1} and the air flow rate was 50 mL min^{-1}.

RESULTS AND DISCUSSION

Thermal Stability of Short Sisal Fibre-ENR/PVC Composite

The DTG and DTA curves of the short sisal fibre-ENR/PVC (20–30/70) composite, ENR/PVC (70/30) blend. ENR vulcanisate and PVC are shown in *Figure 1*.

As shown in *Figure 1*, the degradation reaction of the short sisal fibre reinforced ENR/PVC composite occurred obviously within the temperature of 266°C~282.3°C, during which the total weight loss was 13.5%. The peak temperature of DTG and DTA were 279.2°C and 281.9°C respectively, while the maximum degradation rate reached 20.3% min^{-1}.

The DTG and DTA curves of PVC in *Figure 1* showed that HCl[7] was strongly liberated from PVC within temperature 257.7°C~310.3°C, during which the total weight loss was 46.5%. It is a heat-absorbing reaction, the peak temperatures of DTG and DTA were the same (283.0°C), at which the maximum degradation rate amounted to 15.4% min^{-1}. The DTG and DTA curves of ENR vulcanisate in *Figure 1* showed that ENR was stable below 341°C. The DTG and DTA curves of ENR/PVC blend (70/30) showed that a strong heat-generating degradation reaction occurred within temperature 257.7°C~271.0°C, during which the total weight loss was 15.1%. The peak temperature of DTG and DTA was 264.6°C and 268.5°C, respectively and the maximum degradation rate was 40.5% min^{-1}.

The results stated above indicated that in both short sisal fibre reinforced ENR/PVC composite and ENR/PVC blend, HCl were strongly liberated from PVC after heating, which resulted in an exothermal catalysed reaction of ENR (acid catalysed exothermal reaction[1]) and accelerated the thermal-oxidative degradation of ENR/PVC blend. When the composite was prepared by adding short sisal fibre in ENR/PVC blend, its degradation rate fell while thermal stability rose. Its mechanism may be explained as follows: the PVC in the composite was diluted after the addition of the short sisal fibre so that the effect of PVC on ENR was weakened.

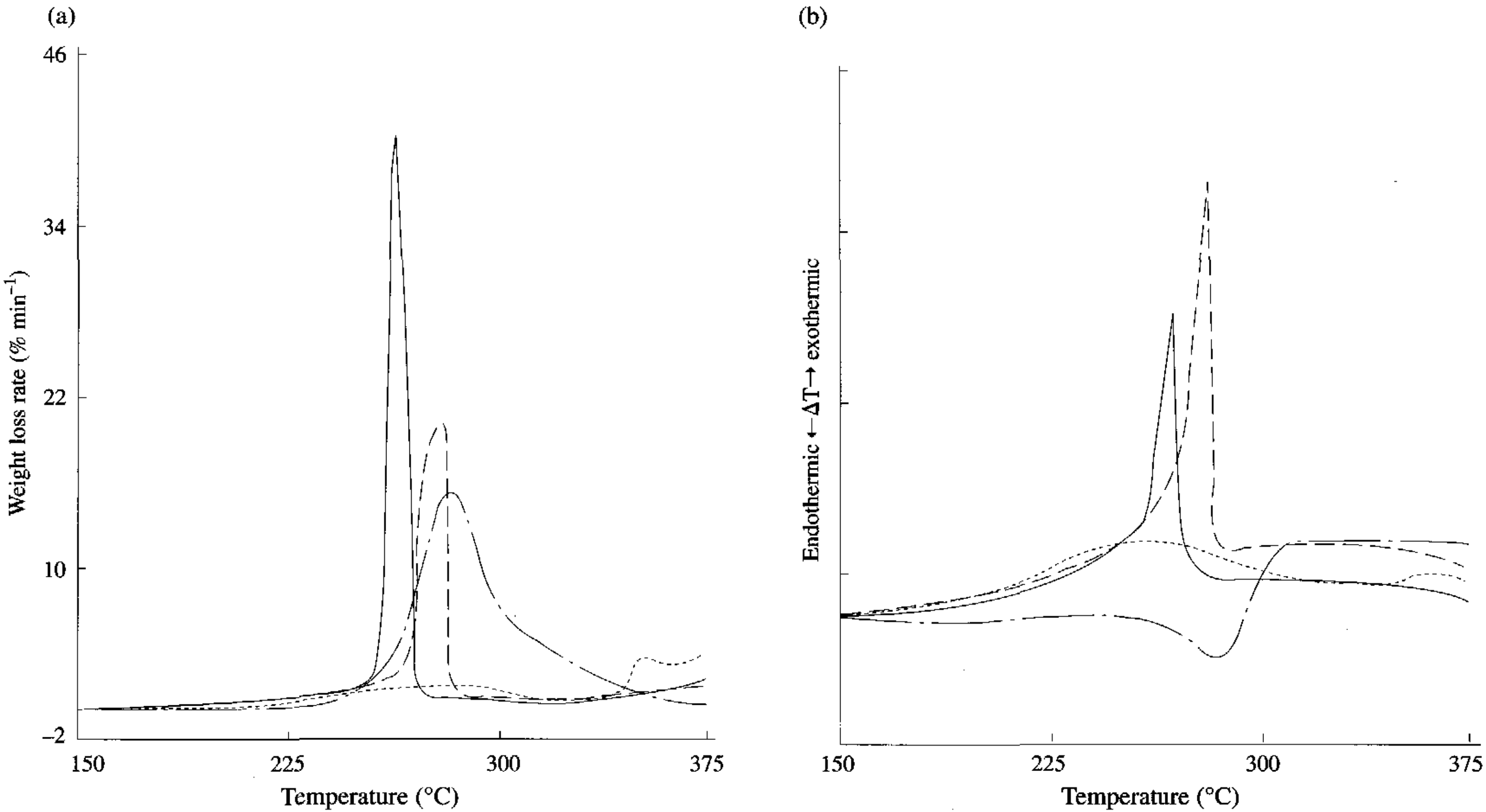

Figure 1. The DTG (a) DTA (b) curves of short sisal fibre reinforced ENR/PVC composite (– – –), ENR/PVC blend (——), ENR (......) and PVC (— · — · — ·).

Influence of the Amount of Short Sisal Fibre on Thermal Stability

Table 3 showed the results of the thermal analysis of the short sisal fibre-ENR/PVC composite. The ratio of ENR and PVC was 80/20 and the amount of the short sisal fibre added was variable. The DTG and DTA peak temperature of the composite and the temperature range in which HCl was strongly liberated all moved towards high temperature with the increasing of the amount of short sisal fibre added, which indicated that the thermal stability of the composite rises with the increasing of the short sisal fibre added.

Influence of the Amount of PVC on Thermal Stability

Table 4 showed the results of the thermal analysis of the short sisal fibre reinforced

TABLE 3. THERMAL ANALYSIS OF THE COMPOSITE CONTAINING ENR/PVC IN RATIO 80/20 AND VARIABLE AMOUNT OF SHORT SISAL FIBRE

Item	Amount of short sisal fibre (p.p.h.)			
	0	20	30	40
Temperature at which strong liberation of HCl (°C) occurred	259.5 – 275.0	267.2 – 282.3	269.4 – 283.4	271.9 – 285.4
Weight loss within the temperature range at which strong liberation of HCl (%) occurred	14.6	13.2	12.6	12.4
Peak temperature of DTG (°C)	268.3	277.7	279.9	282.2
Peak temperature of DTA (°C)	272.1	282.0	283.6	285.2
Maximum degradation rate (% min^{-1})	27.1	18.1	19.3	17.0

TABLE 4. THERMAL ANALYSIS OF THE COMPOSITE CONTAINING 20 P.P.H. OF SHORT SISAL FIBRE AND VARIABLE RATIO OF ENR/PVC

Item	Ratio of ENR/PVC			
	90/10	80/20	70/30	60/40
Temperature at which strong liberation of HCl (°C) occurred	272.8 – 289.3	266.8 – 282.3	266.0 – 282.3	262.9 – 279.8
Weight loss within the temperature range at which strong liberation of HCl (%) occurred	8.7	13.2	13.5	16.2
Peak temperature of DTG (°C)	283.3	277.7	279.2	278.1
Peak temperature of DTA (°C)	285.9	282.0	281.9	279.2
Maximum degradation rate (% min^{-1})	8.0	18.1	20.3	47.9

ENR/PVC composite containing 20 p.p.h short sisal fibre; the ratio of ENR and PVC was variable. The data indicated that the catalysed oxidative degradation of the composite caused by the HCl liberated became stronger with the increasing of the amount of PVC in the composite. The DTG and DTA peak temperature of the composite and the temperature range in which HCl was strongly liberated all moved towards low temperature, the maximum degradation rate accelerated and the weight loss in this temperature range increased with the increasing of the ratio of PVC. These results showed that the thermal stability of the composite fell with the increasing of the amount of PVC added.

CONCLUSION

HCl was strongly liberated from PVC in the composite within the temperature 266.0°C ~ 282.3°C, which resulted in an exothermal catalysed reaction of ENR and accelerated the oxidative degradation of ENR/PVC blend. The addition of short sisal fibre raised the thermal stability of the composite.

The thermal stability of the composite rose with the increasing amount of the short sisal fibre added and fell with the increasing ratio of PVC in the composite.

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