

DAMPING PERFORMANCE OF EUCOMMIA ULMOIDES GUM

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Abstract Eucommia ulmoides gum (EU gum), known as gutta percha in Southeast Asia, is a natural polymer with double characteristics of rubber and plastic. In present paper, $\tan\delta$ - T curve and hysteresis loss (HL) were chosen to characterize its damping property. The results indicated that its $\tan\delta$ value would increase with rising of temperature when $T > 0^\circ\text{C}$ and form another damping peak at 40–80°C besides T_g peak. This phenomenon resulted from meltage of crystals of EU gum could increase its damping property at ambient-high temperature. Its $\tan\delta$ value even exceeded those of conventional damping rubbers, such as nitrile-butadiene rubber (NBR) and chlorinated isobutene-isoprene rubber (CIIR).

Keywords: EU gum; Gutta percha; Crystalline characteristic; Damping property; Hysteresis loss.

INTRODUCTION

Eucommia ulmoides oliv (*E ulmoides*) is a specific plant from the Tertiary Period that has survived only in China^[1]. According to botanists, *E ulmoides* belongs to the family of Eucommiaceae which is the only one family in the world^[2]. Its barks and leaves are very good Chinese herbs for curing hypertension^[3]. However, there is still a kind of natural polymer in its tissues of leaf, bark and seed which is named as eucommia ulmoides gum. China has 95% *E ulmoides* resources of the world, and that will become a large green chemical factory to produce natural polymer material, EU gum, in the future.

Damping is defined as the decay of force imposed or the dissipation of energy of object in movement. Rubber is a kind of ideal damping material for its very good viscoelasticity^[4]. On one hand, it can store energy as elastic material; on the other hand it will dissipate energy as viscous liquid. When rubber material is deformed by force, one part of energy is stored as potential energy; another part of energy is dissipated as heat which characterized its damping behavior. At present, rubber damping materials are applied to many fields, such as aerospace, aviation, ships, precision machinery, construction, automobile industry, etc.

EU gum is a kind of crystalline viscoelastic polymer material. For the past hundreds of years, many chemists^[5–8] had studied its crystalline characteristics and suggested that EU gum had two crystal forms, one was α -form (monoclinic, 64°C), the other was β -form (orthorhombic, 57°C). Yan^[2] had concluded that EU gum had three prominent characteristics: flexible chain, trans-structure, and double-bonds. So EU gum could be vulcanized by conventional cross-linker and its vulcanizate could crystallize at ambient temperature. However, few literatures are found to study the relationship between crystalline and damping properties.

At present, studies^[9] on the dynamic mechanical properties of EU gum focused mainly on its glass transition zone (T_g) and drew a conclusion that its macromolecular chains were flexible and easy to crystallize that would make its $\tan\delta$ values at T_g zone very small. So the heat generated due to the inner friction between macromolecules was very low. As a result, EU gum could be made into green tire which would reduce energy

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consumption and save resources^[10]. However, these studies didn't involve the dynamic mechanical property of EU gum at ambient-high temperatures (T_m). In fact, EU gum shows the second damping mechanism of crystalline meltage transition which was just at ambient-high temperatures (0–100°C). It was different from conventional rubber whose damping mechanism was from glass transition.

In addition, three general rubbers, butadiene rubber (BR), butadiene-styrene rubber (SBR), nature rubber (NR); two polar rubbers, chlorobutadiene rubber (CR), nitrile-butadiene rubber (NBR); two saturated rubbers, ethylene-propylene diene monomer (EPDM), chlorinated isobutene-isoprene rubber (CIIR), have been chosen to compare with EU gum. These rubbers are all noncrystalline rubbers at ambient temperature^[11]. They have special structures, such as big or polar pendant groups, which have great effects on their damping properties. By comparing their damping properties with those of EU gum, a conclusion can be drawn that the crystalline characteristics of EU gum have strong effect on its damping properties.

EXPERIMENTAL

Instrument & Reagent

EU gum was extracted from the seeds of *E ulmoides* by suitable solvent; BR-9000 was produced by Beijing Yanshan Petrochemical Co. Ltd of China; NR was the first grade standard rubber produced by China; SBR-1500 was produced by Shandong Qi-Lu Petrochemical Co. Ltd of China; CR-WRT was produced by Dupont Co. Ltd of USA; EPDM-J-3080 was produced by Jilin Petrochemical Co. Ltd of China; CIIR1068 was produced by Exxon Co. Ltd of USA; NBR-1052 was produced by Nan-Di Co. Ltd of Taiwan. Other additives were all bought in the market.

The main testing machines were XLW-200 minitype electronic extension testing machine which was manufactured by Guangzhou Testing Machine Co. Ltd of China and Dynamic Mechanical Thermal Analyses (DMTA-V) which was manufactured by Rheometric Scientific, Inc of USA.

Preparation and Test of Sample

Vulcanizate sheets of rubbers, 1.5 mm thick, were made by an uniform mixing technology with a standard recipe^[12], vulcanized at 150°C for 30 min and died to suitable test-pieces for testing.

Two parameters were chosen to characterize the damping properties of EU gum. One was $\tan\delta$, tested by DMTA, the other was hysteresis loss (HL), tested by an extensometer.

$\tan\delta$ - T curve was tested by DMTA. The rectangle test-pieces were cut from the vulcanizate sheet of various rubbers with 25 mm in length, 5 mm in width, and 1.5 mm in thickness. The heating rate was 3 K/min, the frequency was 10 Hz, the range of testing temperature was from –100°C to 100°C.

HL (hysteresis loss) was tested in terms of GB1686-85. The sizes of dumbell test-pieces were 25 mm in length, 5 mm in width, and 1.5 mm in thickness. The test temperature was 25°C and 75°C, respectively.

RESULTS AND DISCUSSION

$\tan\delta$ - T Curve of EU Gum

The $\tan\delta$ - T curve of EU gum is shown in Fig. 1. It is seen from the picture that the $\tan\delta$ - T curve of EU gum is very different from that of conventional rubber which has only one T_g peak. EU gum had two peaks in its $\tan\delta$ - T curve, one was T_g peak, the other was T_m peak. It indicated that not only the glass transition but also the crystalline meltage transition could contribute to its damping property. So a conclusion could be drawn that EU gum had two damping mechanisms: one was glass transition damping mechanism, the other was crystalline meltage transition damping mechanism. The latter could endow EU gum with better damping performance at ambient-high temperatures.

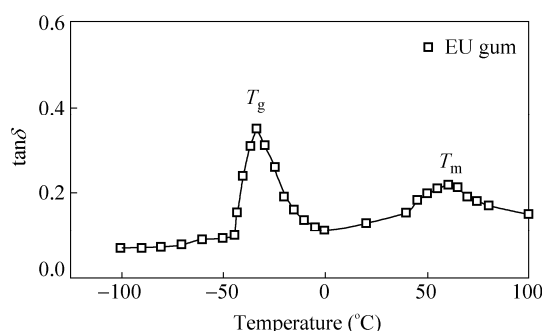


Fig. 1 $\tan\delta$ curve of EU gum

Comparison with NR

NR is the isomer of EU gum. Their $\tan\delta$ - T curves are plotted in Fig. 2 for comparison. As shown in Fig. 2, their $\tan\delta$ - T curves were very different. NR had only one T_g damping peak, but EU gum had double peaks, one was T_g damping peak, the other was T_m damping peak. At T_g damping zone, the envelop area of NR under $\tan\delta$ - T curve was large, but the envelop area of EU gum was small; $T > 0^\circ\text{C}$, the $\tan\delta$ of NR would decrease with temperature increase, but the $\tan\delta$ of EU gum would increase. The only similarity of their $\tan\delta$ - T curves was that they had similar T_g , -35°C (NR) and -33°C (EU gum), and their temperature ranges of T_g were both within -60°C to 0°C as well.

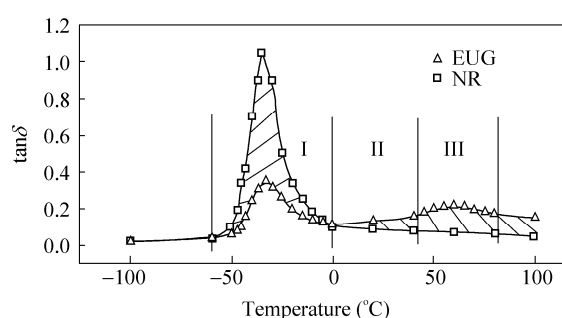


Fig. 2 Damping zones of EU gum and NR

First damping zone I	$-60^\circ\text{C} < T < 0^\circ\text{C}$	$0.04 < \tan\delta < 0.35$
Second damping zone II	$0^\circ\text{C} < T < 40^\circ\text{C}$	$0.1 < \tan\delta < 0.155$
Third damping zone III	$40^\circ\text{C} < T < 80^\circ\text{C}$	$0.155 < \tan\delta < 0.22$

In terms of temperature, the $\tan\delta$ - T curve of EU gum could be divided into three damping zones, as shown in Fig. 2. The first damping zone was at $-60^\circ\text{C} < T < 0^\circ\text{C}$, it was the T_g damping zone; the second damping zone was at $0^\circ\text{C} < T < 40^\circ\text{C}$, the $\tan\delta$ value of EU gum would increase with rising of temperature; the third damping zone was at $40^\circ\text{C} < T < 80^\circ\text{C}$, it was the T_m damping zone. The three damping zones of EU gum were very closely related with crystallinity.

At the first damping zone, the temperature was very low, EU gum was in crystalline state^[13]. However, only part of EU gum could crystallize. The remaining EU gum was still in amorphous state. When temperature reached T_g , chain segments of EU gum in uncrystalline zone were in movement state and contributed to the peak of T_g . But chain segments in crystalline zone of EU gum were still in frost state. It would reduce $\tan\delta$ value of EU gum. So the damping peak of EU gum was much smaller than that of NR. The shade part I in Fig. 2 was the part of $\tan\delta$ value of EU gum reduced by crystallinity. In conclusion, the $\tan\delta$ value would be reduced enormously because of the crystallinity of EU gum in conventional T_g damping zone.

At the second damping zone, the $\tan\delta$ of NR would decrease gradually with temperature increase.

However, the $\tan\delta$ of EU gum would increase, showing the difference with NR. In general, due to the strain of chain segments of viscoelastic macromolecules lagging behind stress under periodic stress, it will generate a phase difference (δ), so the modulus of material at present is a complex modulus,

$$E^* = E' + iE'' \quad (1)$$

and

$$\tan\delta = E''/E' \quad (2)$$

where E' is defined as the energy stored due to the elastic deformation of object under stress and named as storage modulus (Pa); E'' is defined as the energy dissipated as heat in deformation process of object and named as loss modulus (Pa). So the $\tan\delta$ value is controlled by E' and E'' of materials. Figures 3 and 4 plot the storage modulus (E') curves and the loss modulus (E'') curves of NR and EU gum respectively.

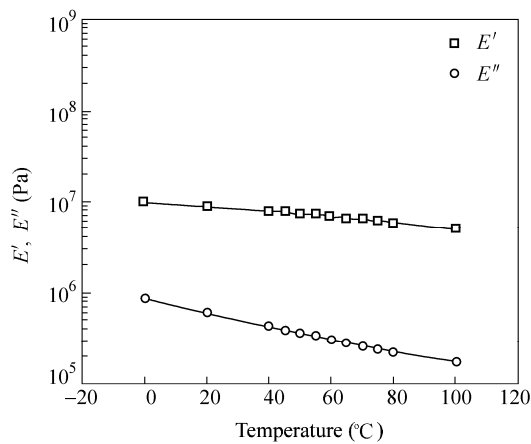


Fig. 3 Curve of E' and E'' of NR

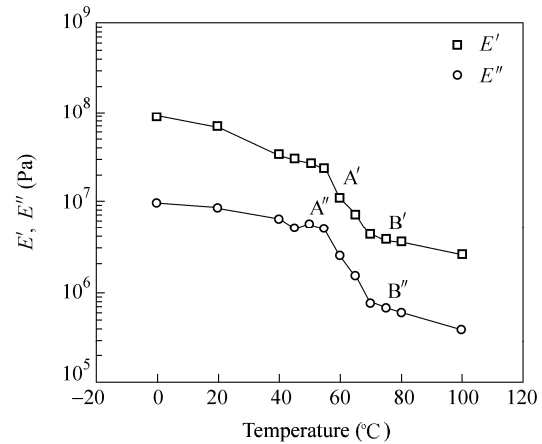


Fig. 4 Curve of E' and E'' of EU gum

It was seen from Fig. 3, in the range of 0–100°C, both E' and E'' of NR decreased, and E''/E' decreased as well. In general, rising temperature could enlarge the space and reduce the intermolecular force between macromolecules which could decrease the hysteresis of chain segments movement. It indicated that temperature had more effect on E'' without the effect of crystal. This also explained why $\tan\delta$ of NR would decrease with temperature increase.

It was seen from Fig. 4, in the range of 0–40°C, E' and E'' of EU gum, like NR, both decreased as well. But E''/E' increased which was contrary to NR. EU gum had two crystal forms, α -form ($T_m = 64^\circ\text{C}$) and β -form ($T_m = 57^\circ\text{C}$). But none of them could crystallize perfectly and existed crystalline defects which were unstable at lower temperatures. It indicated that temperature had more effect on E' under the crystalline condition. When temperature rose, E' decreased more than E'' so that the $\tan\delta$ value of EU gum could increase.

At the third damping zone, three stages could be divided in terms of modulus. The first stage was at 40–57°C, the modulus of EU gum would decrease continuously with temperature increase. Because the irregular crystals would melt first, the storage modulus decreased more. So $\tan\delta$ - T curve of EU gum went upwards. The second stage was at 57–65°C, the temperature reached the crystalline melting point, and the crystal melt rapidly which would make the modulus of EU gum decrease sharply. So the modulus curves of EU gum exhibited inflexion of A', A'', as shown in Fig. 4. In this temperature area, the $\tan\delta$ of EU gum reached the maximum value. The third stage was at 65–80°C, the crystalline zone shrank gradually, and disappeared in the end. The influence of crystal on modulus decreased, and appeared another inflexion of B', B''. It would lead the $\tan\delta$ of EU gum decreased. So the $\tan\delta$ - T curve of EU gum formed a damping peak at 40–80°C.

In fact, EU gum has two types of crystal forms, whose melting points are 57°C and 64°C respectively, so it

should have two damping peaks. But there was only one damping peak in Fig. 2 (shade zone III). This was because the two damping peaks approached closely and superposed together to form one peak only.

The analysis above indicated, the meltage change of crystal could not only increase the $\tan\delta$ value of EU gum, also widen its damping application temperature. The melting points of EU gum were very close to ambient temperature, so EU gum could get better damping property at ambient temperature or higher temperatures.

Comparison with Damping Rubbers at Ambient-high Temperatures

The envelop areas under $\tan\delta$ - T curves of rubbers could characterize their damping performances which showed the difficulty extent of the movement of the chain segments of the rubber macromolecules changing from the glass state to rubber state^[14].

In general, if a polymer material has rigid chain, big or polar side group, its damping property is excellent and vice versa. Because of the bulk effect, CIIR has the biggest envelop area and the best damping property; due to the induction effect, CR has a bigger envelop area and its damping property is better. But their damping peaks are all at glass transition temperature far away from 0°C, and their damping properties are poor when $T > 0^\circ\text{C}$. However, the damping property of EU gum is better when $T > 0^\circ\text{C}$.

The $\tan\delta$ - T curves of EU gum, CR and CIIR at 0–100°C were shown in Fig. 5 for comparison. As shown in Fig. 5, when $T > 0^\circ\text{C}$, the $\tan\delta$ of CIIR and CR all decreased gradually. On the contrary, $\tan\delta$ of EU gum increased with rising of temperature. In addition, its $\tan\delta$ - T curve formed another peak between 40°C and 80°C. Its damping value ($\tan\delta$) exceeded CR when temperature reached 18°C, and even exceeded CIIR when temperature reached 45°C. So EU gum would have better damping property at ambient and high temperatures.

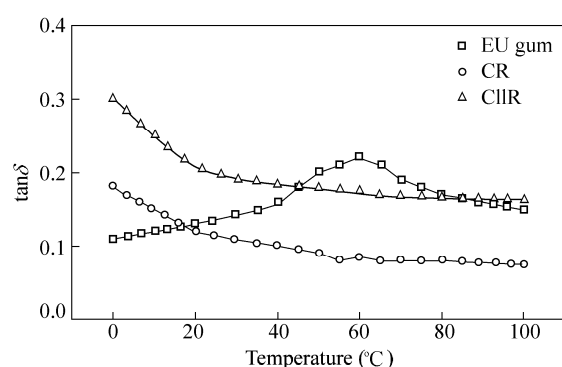


Fig. 5 $\tan\delta$ curves of EU gum, CR and IIR

Hysteresis Loss of EU Gum and Other Rubbers

As shown in Fig. 6 that damping rubber would yield to a hysteresis loop when its test-piece was extended and retracted at a fixed strain. Hysteresis loss (HL) was defined as the ratio of the hysteresis loop area (C) to the area under extension curve (A)^[4]. It could be seen in Fig. 7 that all the elastomers existed a “soft effect of stress^[11]”, so all the rubber vulcanizate test-pieces were extended and retracted for ten times to eliminate the effect.

As shown in Fig. 7 the rubber’s HLs were almost a constant after three times of extension and retraction. So their average HLs were evaluated from the third value to the tenth value. In terms of GB1686-85, HLs of different rubbers at ambient temperature (25°C) could be shown in Table 1. In addition, the $\tan\delta$ values of different rubbers at 25°C are listed below at the same time.

Table 1. HL and $\tan\delta$ of different rubbers at ambient temperature (25°C)

	BR	SBR	NR	CR	EPDM	CIIR	NBR	EU gum
HL (%)	4.48	5.63	5.87	11.77	16.31	17.86	24.24	30.84
$\tan\delta$	0.074	0.0875	0.091	0.1	0.1	0.188	0.16	0.135

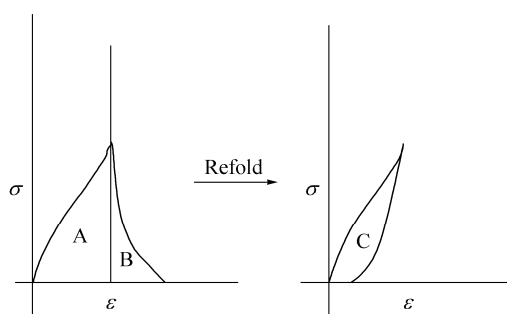


Fig. 6 Hysteresis loop curve produced by extension and retraction curves of rubber

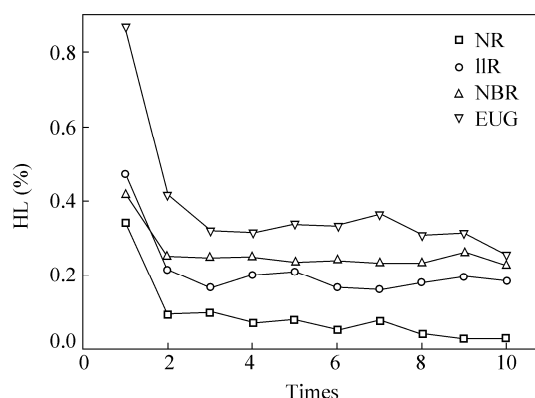


Fig. 7 HL of four rubbers for ten times

It was shown in Table 1, except EU gum, the rubber with bigger side groups or polar side groups would have larger HL. It was consistent with the rule of $\tan\delta$. The HL of EU gum was the maximum in all the tested rubbers. However, the $\tan\delta$ value of EU gum was not the maximum at the ambient temperature. This was related to the crystal and the strain suffered by the EU gum. As known that $\tan\delta$ was obtained under small strain ($\varepsilon = 0.2\%$) which could not change the morphological structure of crystal. So $\tan\delta$ was only controlled by temperature. Ambient temperature was in the second damping zone of EU gum, and its damping property was in the middle. In Table 1, the $\tan\delta$ value of EU gum was equal to 0.135, and it was in the middle as well which responded to its damping property faithfully.

On the contrary, HL was obtained under large strain ($\varepsilon = 200\%$) which could change the morphological structure of crystal. So the HL was not only controlled by temperature but also affected by strain. Under the forced extension of large strain ($\varepsilon = 200\%$), like other rubbers, the uncrystallized part of EU gum vulcanizate could be stretched largely and almost retract completely at ambient temperature. However, the crystalline part of EU gum vulcanizate would deform by forced extension of large strain. This part of deformation could not retract or retract very slowly. It would make the area under extension curve large and the area under retraction curve small. So EU gum could obtain maximum HL value, and could not obtain maximum $\tan\delta$ value at ambient temperature. In other words, if HL was tested under small strain ($\varepsilon = 0.2\%$), the same result could be obtained as that of $\tan\delta$.

All of the test-pieces mentioned above were tested once more at high temperature (75°C), the results are shown in Table 2. Compared with Table 1, we could see that the HL of EU gum decreased, but it was still the largest among all samples. Its $\tan\delta$ value increased and was also the largest. At high temperatures, the crystals disappeared, so the retraction could not be constrained by the crystal any more. So rising temperature would reduce the HL value of EU gum. But the phase change of crystalline melting could contribute to the damping property of EU gum.

Table 2. HL and $\tan\delta$ of different rubbers at high temperature (75°C)

	BR	SBR	NR	CR	EPDM	CIIR	NBR	EU gum
HL (%)	8.6	8.47	12.9	9.34	10.32	11.57	12.57	19.14
$\tan\delta$	0.071	0.065	0.067	0.07	0.11	0.167	0.179	0.2

CONCLUSIONS

From the analysis above, we could know that EU gum had two damping mechanism: conventional glass transition damping mechanism and crystalline melting transition mechanism. In terms of temperature, $\tan\delta$ - T curve of EU gum could be divided into three zones, T_g damping zone ($-60^\circ\text{C} < T < 0^\circ\text{C}$), the damping transitional zone at ambient temperature ($0^\circ\text{C} < T < 40^\circ\text{C}$) and T_m damping zone ($40^\circ\text{C} < T < 80^\circ\text{C}$),

respectively. From 25°C–75°C the process of phase change of crystal of EU gum could increase its damping property. Its $\tan\delta$ value, at 75°C, even exceeded that of conventional damping rubbers, such as NBR and CIIR.

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