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Dynamic mechanical properties of *Eucommia ulmoides* gum with different degree of cross-linking

Sarina · Jichuan Zhang · Liqun Zhang

Abstract　The dynamic mechanical properties of *Eucommia ulmoides* (EU) gum with different degree of cross-linking are studied systematically in this article. EU gum displays five dynamic mechanical behaviors with increasing degree of cross-linking. Before elastic critical turning point, EU gum shows two active dynamic mechanical temperature zones with rising of temperature, one is T_g zone, controlled by glass transition mechanism, the other is T_m zone, controlled by crystalline melting mechanism, its tan δ values at T_g zone and T_m zone during the process of cross-linking obey the dynamic reverse transition law: at the T_g zone, the peak value of its tan δ is proportional to cross-linking degree inversely proportional to crystallinity degree; at T_m zone, its tan δ value is proportional to crystallinity degree and inversely proportional to cross-linking degree. In addition, the T_g, T_m, and X_c of the EU gum with different degrees of cross-linking are obtained as well.

Keywords　*Eucommia ulmoides* gum · Gutta percha · tan δ ·
Dynamic mechanical property · DMTA

Introduction

EU gum is a natural crystalline polymer extracted from the tissues of *Eucommia ulmoides* Oliver which is the same polymer called as gutta percha extracted form *Palaquium gutta* grown in Southeast Asia [1, 2]. Its chemical formula is trans-1,4-polyisoprene which is an isomer of natural rubber with characteristics of both rubber and plastic [3–5], as shown in Fig. 1. To date, most studies on EU gum have focused only on its crystalline characteristics [6–9]. Few studies about its dynamic mechanical properties have been reported [10]. Actually, the dynamic mechanical

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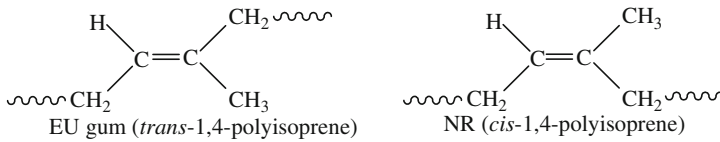e-mail: zhjc75@126.com

Fig. 1 Macromolecular structure of EU gum and NR

properties of EU gum are very complicated. First, it is easy to crystallize because of its regular macromolecular chain. Second, EU gum can be cross-linked into a network structure because of its double bonds [1], and no melt flow occurs although the temperature exceeds melting point. So the dynamic mechanical properties of EU gum are controlled by both glass transition and crystalline melting mechanisms. In turn, these two mechanisms are simultaneously controlled by the degree of cross-linking and degree of crystallinity.

Dynamic mechanical thermal analysis (DMTA) is usually used to study the modulus and damping of polymeric materials in strained states caused by periodic alternating stress. The damping of polymer materials is defined as the tangent of the phase differences in stress and strain, and it is designated as mechanical loss. Mechanical loss is equal to the ratio of loss modulus and storage modulus of polymer materials [11], namely:

$$\tan \delta = E''/E' \tag{1}$$

$\tan \delta$, E'', and E' are the characteristic quantity related to the mechanical relaxation of polymeric materials. They are very sensitive to glass transition, crystallization, cross-linking, phase separation, and other subrelaxation processes [12, 13]. In this article, $\tan \delta$, E'', and E' are used to characterize the dynamic mechanical properties of EU gum. In addition, the changes in the dynamic mechanical properties of EU gum are studied by controlling the temperature and the cross-linking degree of EU gum.

Experimental

Materials

EU gum was extracted from the seeds of *E. ulmoides* Oliver. Further details concerning the extraction can be found elsewhere [14, 15]. Dicumyl peroxide (DCP) was bought from Shanghai Jiachen chemical Co., Ltd.

The two-roll mill (XK-160) was used to introduce DCP into the EU gum, and the roller temperature was 85 ± 5 °C. First, the EU gum was placed on two-roll mill, and mixed for 5 min until the rubber fully covered from the roll. DCP was added into the EU gum and was evenly mixed. The two-roll mill was then stopped, the mixed EU gum was left to stand for 24 h, and was cross-linked by a plate vulcanizing machine at 150 °C for 30 min. Finally, the cross-linked sheet of

EU gum, 1.5 mm thick, which was mixed with different DCP, was died to suitable test-piece for testing.

Rectangular samples, $25 \times 5 \times 1.5$ mm^3, were cut from the cross-linked sheet with different cross-linking degrees for DMTA testing.

Rectangular samples, $15 \times 15 \times 1.5$ mm^3, were cut from the cross-linked sheet with different cross-linking degrees for WAXD testing.

Dynamic mechanical thermal analyses (DMTA)

All tan δ–T and modulus–T curves of the EU gum with different degrees of cross-linking were tested by DMTA (DMTA-V Rheometric Scientific). The heating rate was 3 °C/min at a frequency was 10 Hz and the testing temperature ranged from −100 to 100 °C.

Differential scanning calorimetry (DSC)

The melting points of EU gum with different degrees of cross-linking were tested by DSC (DSC1 Mettler-Toledo). The testing temperature ranged from −10 to 100 °C at a heating rate of 10 °C/min.

Wide angle X-ray diffraction (WAXD)

The crystalline structures of EU gum with different degrees of cross-linking were tested via WAXD (WAXD-D/max2500 Rigaku). Cu (Kα1), $\lambda = 1.54056$ Å, $5° < 2\theta < 30°$, and scan rate 3°/min.

Results and discussion

The dynamic mechanical property of EU gum is very sensitive to two factors: temperature and cross-linking. These two factors are also the key means to control the crystalline behavior of EU gum [14]. With rising of cross-linking degree, EU gum displays five dynamic mechanical behaviors. With rising of temperature, EU gum shows two active dynamic mechanical temperature zones: T_g and T_m, respectively.

Dynamic mechanical properties of EU gum in different degree of cross-linking

Dynamic mechanical properties of EU gum without cross-linking

EU gum is a semi-crystalline polymer [16, 17], its aggregate structure is chiefly composed of crystalline and amorphous zones [18, 19], and melting flow can occur when temperature exceeds T_m if EU gum is not cross-linked. The modulus–T curves and tan δ–T curve of EU gum without cross-linking (DCP = 0 phr) are plotted in Fig. 2. As shown in Fig. 2, at the T_g zone, the movement of the molecular segments of EU gum in the crystalline zones is greatly restricted, only a small parts of the
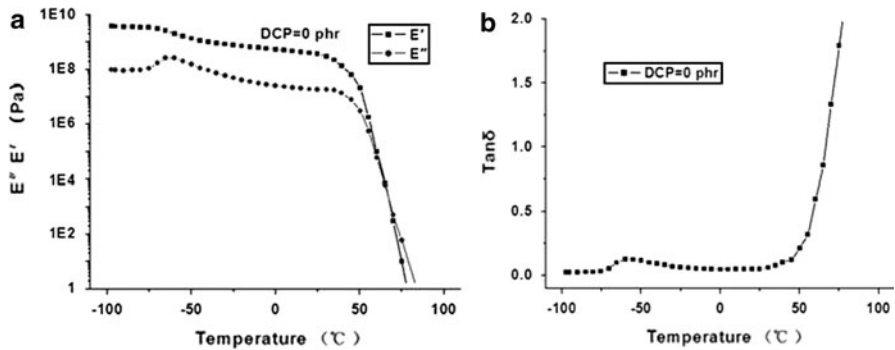
Fig. 2 Modulus–T curves and tan δ–T curve of EU gum without cross-linking

molecular segments of EU gum in amorphous zone can move freely, so the E'–T curve decreases very little, and the E''–T curve only shows a small bump with rising of temperature, as a result, the rubber plateau is not very obviously, and the peak shape of the tan δ–T curve of EU gum at T_g zone is very small. At the T_m zone, the crystals melt and there are some physical entanglements in EU gum, the sample changes into viscous liquid, so E'–T curve and the E''–T curve decrease rapidly and tend to 0 Pa with rising of temperature, but storage modulus decrease more sharply than loss modulus, as a result, the phase difference between strain and stress is close to 90°, $\tan \delta = \frac{E''}{E'} = \frac{\sin\delta \to 1}{\cos\delta \to 0}$, so the tan δ–T curve of EU gum at T_m zone tends to infinity.

Dynamic mechanical properties of EU gum with slight cross-linking

If EU gum is cross-linked by a small amount of DCP, the cross-linking points formed are not enough to form a whole cross-linked network structure, only some local cross-linked network structures are formed which greatly increase the viscosity of EU gum, so plastic flow can no longer occur when temperature exceeds T_m, and EU gum is in a viscous slip state under the external force.

The modulus–T curves and tan δ–T curves of EU gum with slight cross-linking (DCP = 0.2–0.8 phr) are plotted in Fig. 3. As shown in Fig. 3, at the T_g zone, because the crystallization is still dominant, the modulus–T curves is similar to that of EU gum without cross-linking, the tan δ–T curves of EU gum still show small peaks, but the peak values slightly increase with increasing degree of cross-linking. In addition, its T_g temperatures also slightly move toward higher temperature with increasing degree of cross-linking. At the T_m zone, the modulus–T curves first decrease rapidly, then take a turn at 53 °C, and then decrease slowly with rising of temperature. When $T < 53$ °C, the storage modulus decrease more sharply than loss modulus, when $T > 53$ °C, the storage modulus still decrease more quickly than loss modulus. As a result, the tan δ–T curves first increase rapidly, then slowly tend to infinity with rising of temperature, and the inflection points are also observed at 53 °C. The more DCP added, the lower the inflection point, and the slower the tan δ–T curves after the inflection points move to infinity.
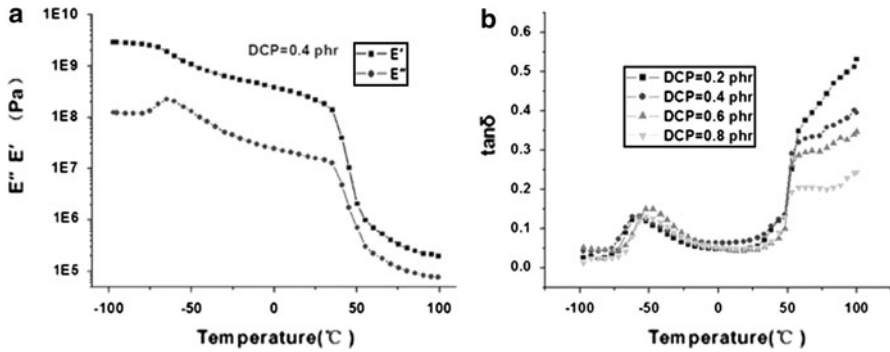
Fig. 3 Modulus–*T* curves and tan δ–*T* curves of EU gum with slight cross-linking

When DCP = 0.8 phr, the tan δ–*T* curve after the inflection point is flat, which indicates that EU gum forms a whole cross-linked network structure, and its tan δ–*T* curve at T_m zone gradually changes into a peak shape.

Dynamic mechanical properties of EU gum with medium cross-linking

If EU gum is cross-linked by sufficient DCP, a whole cross-linked network structure is formed, and the EU gum is in an elastic state when temperature exceeds T_m [20, 21]. The modulus–*T* curves and tan δ–*T* curves of EU gum with medium cross-linking (DCP = 1–2 phr) are plotted in Fig. 4. As shown in Fig. 4, at the T_g zone, the *E′*–*T* curve decreases continuously and the peak of the *E″*–*T* curve increase further with increasing degree of cross-linking, as a result, the rubber plateau is clear, and the peak value of tan δ–*T* curves further increases with increasing degree of cross-linking. At the T_m zone, the modulus–*T* curves first decrease sharply, then show the inflection points at 50 °C, and then decrease slowly with rising of temperature. Before the inflection points, the *E′*–*T* curve decreases more sharply than the *E″*–*T* curve, after the inflection points, the *E″*–*T* curve decrease more quickly than the *E′*–*T* curve. As a result, the shape of the tan δ–*T* curves shows the
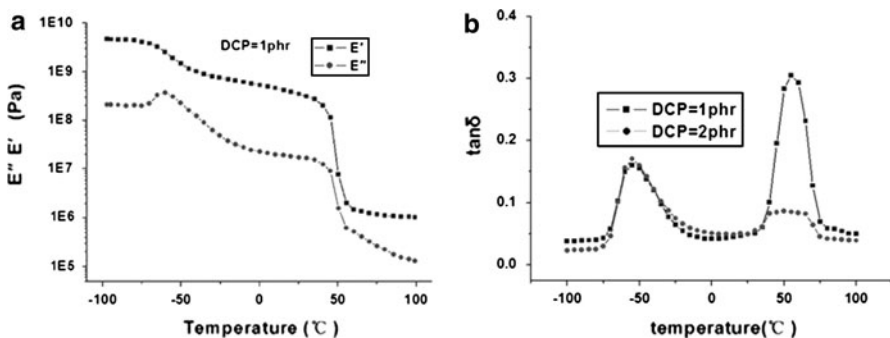

Fig. 4 Modulus–*T* curves and tan δ–*T* curves of EU gum with medium cross-linking

tan δ peak value at 50 °C, which gradually decreases with increasing degree of cross-linking.

In addition, when DCP = 1 phr, the peak value of EU gum at T_g zone is smaller than that of T_m zone. However, when DCP = 2 phr, the peak value of EU gum in the T_g zone is larger than that of T_m zone. It indicates that cross-linking can greatly break the crystallization of EU gum.

Dynamic mechanical properties of EU gum with high cross-linking

The crystallization of EU gum is greatly destroyed if EU gum has a very high degree of cross-linking. The modulus–T curves and tan δ–T curves of EU gum with high cross-linking (DCP = 4–8 phr) are plotted in Fig. 5. As shown in Fig. 5, at the T_g zone, the E'–T curve decreases further and the peak of the E''–T curve increase further with increasing degree of cross-linking, as a result, the peak values in the tan δ–T curve significantly increase with the degree of cross-linking. At the T_m zone, the modulus–T curves first decrease sharply, then show the inflection points at 47 °C, and then decrease slowly with rising of temperature. Before the inflection points, the E'–T curve decrease more sharply than the E''–T curve, after the inflection points, the E'–T curve decrease more slowly than the E''–T curve. As a result, the tan δ–T curves of EU gum do not show the T_m peak but the degressive step instead with rising of temperature. The more DCP added, the deeper the step decreased, and the lower the temperature that shows the degressive step.

Dynamic mechanical properties of EU gum with elastic cross-linking

If the cross-linking degree reaches the elastic critical turning point [14], the crystallization of EU gum disappears completely, and EU gum changes into an elastomer at ambient temperature. And its dynamic mechanical behaviors are similar to that of conventional vulcanized rubber, such as NR. The modulus–T curves and tan δ–T curves of EU gum with elastic cross-linking (DCP $\geq$ 10 phr) are plotted in Fig. 6. As shown in Fig. 6, at the T_g zone, the E'–T curve first decrease
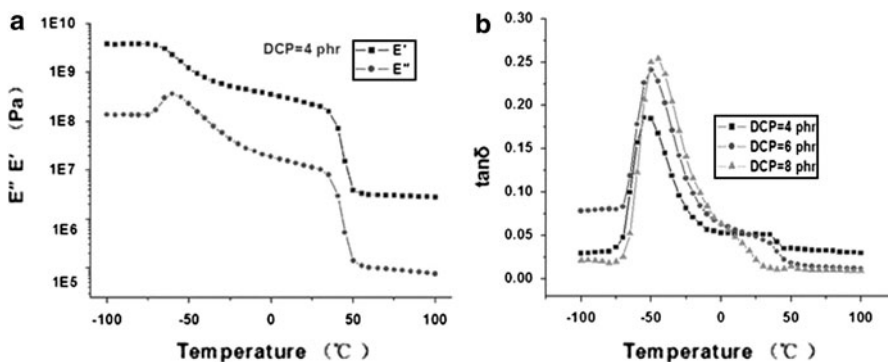

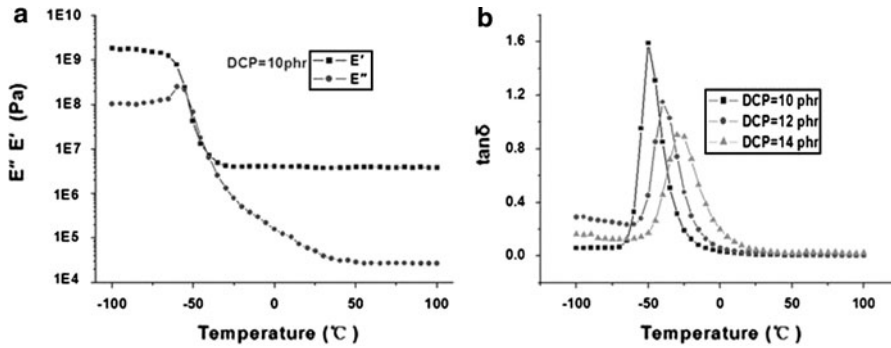**Fig. 5** Modulus–T curves and tan δ–T curves of EU gum with high cross-linking

Fig. 6 Modulus–T curves and tan δ–T curves of EU gum with elastic cross-linking

sharply, then show an inflection point at −55 °C, and then decrease very slowly with rising of temperature, the E'–T curve enters into the rubber plateau zone after the inflection point; however, the E''–T curve first decrease rapidly, then decrease slowly with rising of temperature, and no longer show inflection point. As a result, the peak value of the tan δ–T curve tremendously increases to maximum. Similar to traditional rubber, the tan δ peak values of EU gum gradually decrease with further increases in the degree of cross-linking. Under the condition of elastic cross-linking, both the modulus–T curves and the tan δ–T curves of EU gum don't show the T_m zone any longer.

Discussion of the relationship between DSC and tan δ–T curve of EU gum

Figure 7 shows the DSC curves of EU gum at different DCP dosages. At DCP = 1 phr, the DSC curve of EU gum has two melting peaks, but its tan δ–T curve has only one damping peak. This phenomenon can be explained by the overlap of the two T_m melting peak. At DCP = 4–6 phr, the DSC curves of EU gum still have a melting peak, but the T_m peak of the tan δ–T curve disappears and is replaced by a

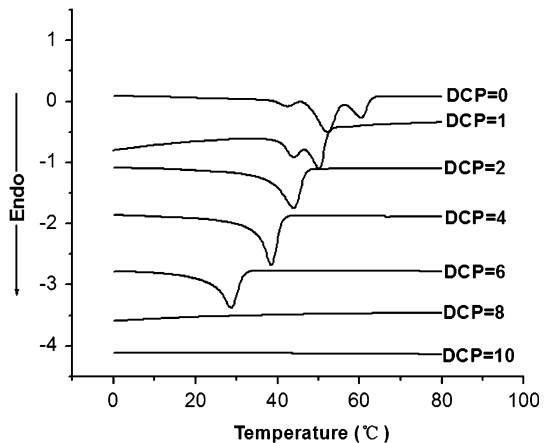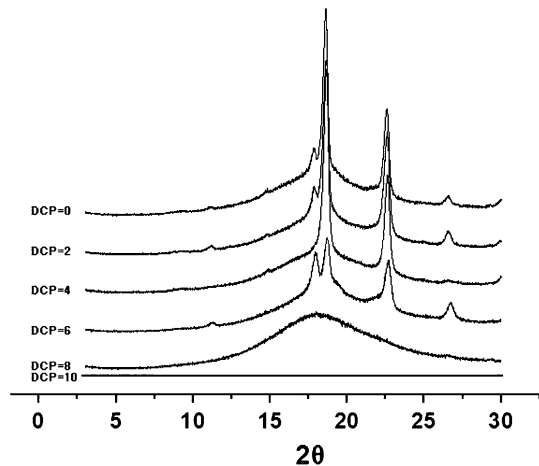**Fig. 7** DSC curves of EU gum with different cross-linking degree

Fig. 8 WAXD spectra
of EU gum with different
degrees of cross-linking

degressive step, as shown in Fig. 5. This is because that EU gum is vulcanized at 150 °C for 30 min, its macromolecules are in the amorphous state at such high temperature. After vulcanization, the macromolecules tend to crystallize with gradual temperature decrease. However, because the degree of cross-linking of EU gum is very high, many cross-linkages hinder EU gum macromolecules from reentering the crystalline lattice. As a result, the macromolecules have to keep in a stressed state to crystallize, this is so called cross-linked internal stress. So its crystalline structure is very loose. When temperature increases to T_m, the EU gum macromolecules immediately change into an elastic disordered state under cross-linked internal stress. The internal friction is very small and the tan δ values are even smaller than that of EU gum before melting. Therefore, the tan δ–T curves of EU gum show degressive steps and no longer show a peak shape. However, at DCP = 8 phr, the DSC curve has no melting peak, but its tan δ–T curve still shows a small degressive step (Fig. 5). This indicates that microscopic domains still remain in the EU gum.

The results of DSC can be verified by the WAXD spectra of EU gum. As shown in Fig. 8, there are two main sharp peaks in the WAXD spectra of EU gum, which are $2\theta = 18.7$ and $2\theta = 22.7$, respectively. With increasing degree of cross-linking, the two peaks gradually become smaller, which indicates that the degree of crystallinity of EU gum gradually decreases. At DCP = 8 phr, the two main peaks basically disappear and only a flat amorphous peak remains, indicating that crystallization of EU gum has almost disappeared.

T_g, T_m, and X_c of the EU gum at different DCP

Wu and co-workers [14] determined the degree of cross-linking ($\overline{M_c}$) of EU gum at different DCP by equilibrium swelling. The results show that the degree of cross-linking gradually decreases with increasing DCP content. EU gum changes into an elastomer when the degree of cross-linking reaches the critical elastic turning point ($\overline{M_c} = 2,900$).

Table 1 T_g, T_m, and X_c of EU gum with different degrees of cross-linking

Content of DCP (phr)	T_g/°C (DMTA)	T_m/°C (DSC)		X_c/% (WAXD)
		α	β	
0	−57.9	60.2	52.1	37.6
1	−55.9	50.3	43.7	–
2	−53.2	43.76	–	31.3
4	−50.8	38.4	–	23.7
6	−48.7	28.6	–	15.2
8	−46.8	–	–	0.42
10	−45.4	–	–	0
12	−40.11	–	–	0
14	−27.7	–	–	0

The glass transitional temperature T_g (determined by DMTA), melting temperature T_m (determined by DSC), and degree of crystallinity X_c (calculated by peak area of WAXD spectra) of EU gum with different degrees of cross-linking are listed in Table 1. As shown in the Table, the T_g temperature of EU gum increases with degree of cross-linking. The T_m temperature decreases with increase in the degree of cross-linking degree. At DCP = 0–1 phr, EU gum has two melting points, corresponding to the alpha and beta forms. At DCP = 2–6 phr, EU gum has only one melting point. At DCP $\geq$ 8 phr, the melting point of EU gum completely disappears. Its X_c decreases with increasing degrees of cross-linking, at DCP = 8 phr, X_c = 0.42%, which indicates it is close to the critical points, from the crystalline cross-linking network to the amorphous cross-linking network. This is consistent with the result of the tan δ–T curve (DCP = 0.8 phr) which has a small degressive step at T_m zone.

Two active dynamic mechanical temperature zones

As shown in Fig. 9, as analyzed above, before elastic critical turning point [14], EU gum with different degree of cross-linking show two active dynamic mechanical temperature zones with rising of temperature: the T_g zone controlled by glass transition and the T_m zone controlled by melting of crystals. In addition, a transitional temperature zone (0 °C < T < 40 °C) is in between T_g and T_m zones which is controlled by crystallization and cross-linking. As shown at the top right corner of Fig. 9, when the degree of cross-linking is small (DCP < 2 phr), the crystallization is dominant, and the tan δ–T curves of EU gum increase with increasing temperature, when the degree of cross-linking is medium (DCP = 2 phr), the effect of crystallization is equal to that of cross-linking and the tan δ–T curve of EU gum is very stable and does not change with temperature increase, when the degrees of cross-linking is high (DCP > 2 phr), the cross-linking is dominant and the tan δ–T curves of EU gum decrease with increasing temperature.
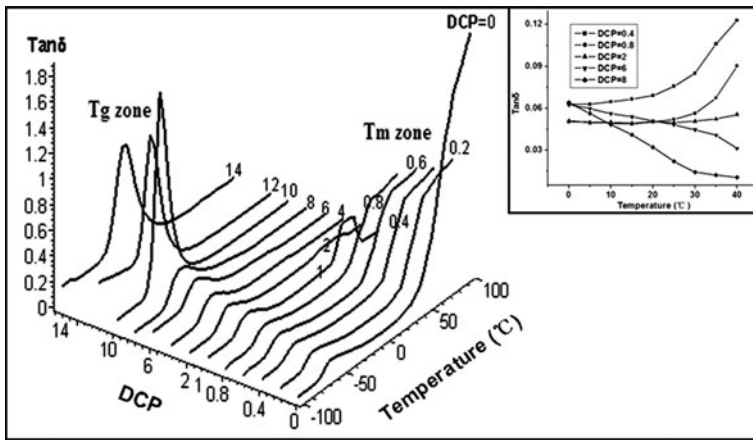
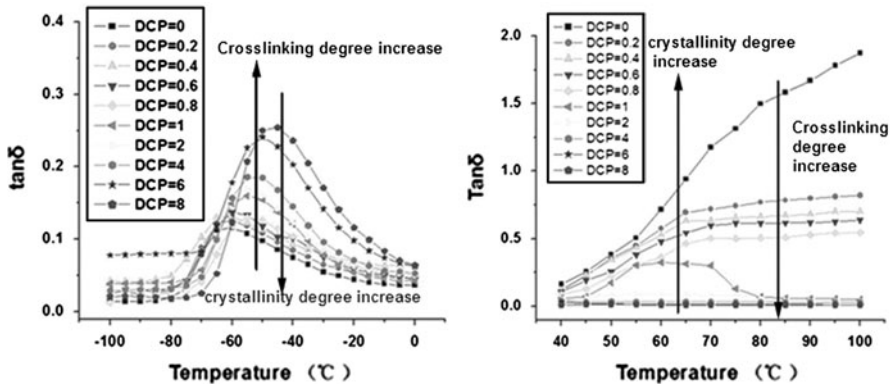**Fig. 9** Three-dimensional tan δ–T curves of EU gum in different cross-linking degree

Fig. 10 Relationship of tan δ value of EU gum at T_g zone and T_m zone with different degree of cross-linking

The change of the tan δ values of EU gum at T_g and T_m is reversed with increasing degree of cross-linking. As shown in Fig. 10, if the tan δ value of EU gum at T_g zone increases, then the tan δ value of EU gum at T_m zone decreases, and vice versa. At the T_g zone, the tan δ value of EU gum increases with increasing degree of cross-linking, and decreases with increasing degree of crystallinity. At the T_m zone, the tan δ value of EU gum decreases with increasing degree of cross-linking, and increases with increasing degree of crystallinity. Therefore, the tan δ value of EU gum in the T_g and T_m zones during cross-linking obeys the dynamic reverse transition law, see below:

$$\tan \delta \propto V/X_c \, (-70\,°C < T < 0\,°C) \tag{2}$$

$$\tan \delta \propto X_c/V \, (40\,°C < T < 80\,°C) \tag{3}$$

where V is the degree of cross-linking and X_c is the degree of crystallinity.

Conclusions

Traditional view shows that the damping properties of polymeric materials can only be evaluated by their tan δ values in the T_g zone. The results of this article indicate that the damping properties of polymer materials can be evaluated using their tan δ values at both the T_g and T_m zones if the polymer materials can crystallize. This is a supplement to the theory of damping of polymer materials. Most of the damping polymer materials, such as rubber, only possess good damping properties at lower temperatures. However, polymeric damping materials are required to have good damping properties at ambient or even higher temperatures. The melting point of EU gum is at a medium temperature, which may provide it with a wider range of applications.

References

1. Yan RF (1996) Polymeric materials encyclopedia. In: Salamone JC (ed) *Eucommia ulmoides* gum, vol 3. CRC Press, Boca Raton, p 2291
2. Tangpakdee J, Tanaka Y, Shiba KI, Kawahara SC, Sakurai K, Suzuki Y (1997) Structure and biosynthesis of *trans*-polyisoprene from *Eucommia ulmoides*. Phytochemistry 45(1):75
3. Chaturvedi PN (1992) Multiple melting due to secondary crystallization in polymers. J Mater Sci Lett 11(24):1692
4. Cooper W, Vaughan G (1963) Melting transitions in diene polymers. J Polym Sci A 1:159
5. Kuo CC, Woodword AE (1982) Crystallization of *trans*-1,4-polyisoprene. J Polym Sci 20(9):1669
6. Anandakumaran K (1983) Noncrystalline component in dilute-solution-grown crystals of *trans*-1,4-polyisoprene. Macromolecules 16:563
7. Cooper W, Vaughan G (1963) Crystallization of gutta percha and synthetic *trans*-1,4-polyisoprenes. Polymer 4:329
8. Mandelkern L, Quinn F Jr, Roberts AD (1956) Thermodynamics of crystallization in high polymers: gutta percha. J Am Chem Soc 78(5):926
9. Su FY, Liu LZ, Zhou EL, Huang JY, Qian RY (1998) High resolution electron microscopy study of single chain single crystals of gutta percha. Polymer 39:5053
10. Cerveny S, Zinck P, Terrier M, Arrese-Igor S, Alegria A, Colmenero J (2008) Dynamics of amorphous and semicrystalline 1,4-*trans*-poly(isoprene) by dielectric spectroscopy. Macromolecules 41(22):8669
11. Capps RN, Beumel LL (1990) Sound and vibration damping with polymers. In: Corsaro RD, Sperling LH (eds) ACS symposium series, vol 424, Chap 4. American Chemical Society, Washington, DC, p 632
12. Thormann E, Evans DR, CraigVincent SJ (2006) Experimental studies of the dynamic mechanical response of a single polymer chain. Macromolecules 39:6180
13. Sanchis A, Prolongo MG, Masegosa BM, Rubio RG (1995) Dynamic-mechanical study of the dynamics of polymer blends near the glass transition. Macromolecules 28:2693
14. Qian RY, Wu ZC, Xue ZH, Yan RF (1995) Length of chain segment motion needed for crystallization. Macromol Rapid Commun 16:19–22
15. Zhang XJ, Cheng C, Zhang M, Lan XY, Wang QH, Han SF (2008) Effect of alkali and enzymatic pretreatments of *Eucommia ulmoides* leaves and barks on the extraction of gutta percha. J Agric Food Chem 56:8936
16. Boochathum P, Chiewnawin S (2001) Vulcanization of *cis*- and *trans*-polyisoprene and their blends: crystallization characteristics and properties. Eur Polym J 37(3):429
17. Boochathum P, Chiewnawin S (2001) Vulcanization of *cis*- and *trans*-polyisoprene and their blends: cure characteristics and crosslink distribution. Eur Polym J 37(3):417

18. Boochathum P (1993) Structure of solution-grown *trans*-1,4-polyisoprene crystals: 3. Thermodynamic properties of α-TPI crystals. Polymer 34(17):3699
19. Pathak A, Saxena V, Tandon P, Gupta VD (2006) Vibrational dynamics of *trans*-1,4-polyisoprene (*β*-form). Polymer 47(14):5154
20. Barrie JA, Standen J (1967) Thermoelastic measurements on some elastomers. Polymer 8:97
21. Mark JE (2003) Some unusual elastomers and experiments on rubberlike elasticity. Prog Polym Sci 28(8):1205