Polym. Bull. (2011) 67:511–525
DOI 10.1007/s00289-011-0489-9

ORIGINAL PAPER

Study on under-water sound absorption properties of *Eucommia ulmoides* gum and its blends

Jichuan Zhang · Zhaohong Xue

Received: 16 October 2010 / Revised: 24 March 2011 / Accepted: 14 April 2011 /

Abstract The sound absorption performances of *Eucommia ulmoides* (EU) gum and its blends with conventional damping rubber are studied systematically. Blending 20%, 40% EU gum into chlorobutadiene rubber (CR), their under-water sound absorption property at 3–20 kHz is better obviously than that of CR. Blending 10, 20, 30, and 40% EU gum into chlorinated isobutene-isoprene rubber (CIIR), their sound absorption properties at 3–20 kHz are also better obviously than those of CIIR, especially the SAC of EU gum/CIIR (20/80) at 3 kHz is equal to 76% which is a great increase at low frequency region. The results show that a critical blend ratio of EU gum exists which is equal to 50%, if EU gum >50%, their under-water sound absorption properties are very poor, if EU gum <50%, their under-water sound absorption properties are very good. The relaxation absorption of damping rubber, the spacial diffuse reflection absorption of EU gum crystallites, and the shear deformation absorption in the interface between crystalline hard phase and rubber soft phase are the three main reasons to contribute their under-water sound absorption properties. In addition, reducing crosslinking degree can increase under-water sound absorption property.

Keywords *Eucommia ulmoides* gum · Gutta percha · Tanδ · Dynamic mechanical properties · Acoustic properties · Sound absorption coefficient

Introduction

Rubber is endowed with extensive application at acoustics field by its superior acoustic characteristic [1, 2]. As under-water sound absorption material, it must obey two essential principles [3]: one is that the acoustic impedance of material must match that of water so that the sound wave could enter into the material

---

J. Zhang (✉) · Z. Xue
Institute of Chemistry Chinese Academy of Science, Beijing 100190, China
e-mail: zhjc75@126.com

successfully; the other is that the material must possess enough mechanical loss so that the sound wave could be dissipated as heat adequately when it transmits in the material. The acoustics impedances of most of rubbers can match that of water, and can not match that of air. So rubber could be used as sound absorption materials in the water, and used as sound insulation materials and shock absorption materials in the air [4].

The sound energy is dissipated mainly by three ways [5, 6]: viscous absorption, heat conduction absorption, and relaxation absorption of sound wave. The viscous absorption of sound wave depends mainly on the density of medium. As the density of rubber materials is about one thousand times than that of air, the viscous absorption of sound wave in rubber medium is much less than that of air. As the rubber is poor conductor of heat, the heat conduction absorption of sound wave in rubber is not obvious as well [1]. However, rubber is a kind of viscoelastic material which has bigger mechanical loss factor [7], so the relaxation absorption of sound wave become the main way of acoustic attenuation in rubber. However, the relaxation absorption of sound wave is much less than that of the two former acoustic attenuation models mentioned above. In order to improve acoustic absorptivity, rubber material must be modified by its chemical and physical properties and designed by its sound absorption structure [4]. These two methods all can greatly increase the acoustic absorptivity of rubber materials.

EU gum, known as gutta percha in Southeast Asia, is a natural polymer with double characteristics of rubber and plastic [8–11]. The damping property of EU gum is doubly controlled by glass transition mechanism and crystalline melting mechanism. Unlike the conventional rubbers who have only one T_g damping zone, EU gum has three damping zones which are T_g damping zone, T_m zone, and their transitional zone, respectively. Its damping property would increase with rising of temperature at 0–40 °C and even exceed that of Chlorinated Butyl Rubber (CIIR) at 40–80 °C. By experiment we find that mixing a certain amount of EU gum into conventional damping rubbers can effectively increase their acoustic absorptivity, and broaden their scope of sound absorption frequency band, especially at low frequency region.

Experiment

Materials

EU gum was extracted from the seeds of *Eucommia ulmoides* oliv, and further details concerning the extraction can be found elsewhere [12, 13]. Natural Rubber (NR) was first grade smoke sheet rubber produced by Indonesia; Chlorobutadiene (CR-WRT) was produced by Dupont Co. Ltd of USA; Chlorinated Butyl Rubber (CIIR-1068) was produced by Exxon Co. Ltd of USA. Other additives were all bought in the market.

Preparation of sample

The samples of NR, EU gum, CR, CIIR, and the blends of EU gum/CR and EU gum/CIIR are prepared by the uniform mixing technology with a standard recipe [14]. Vulcanizate sheets, 1.5 mm in thickness, were made by a vulcanization process of 150 °C × 30 min, and were died to suitable test-pieces for testing. Vulcanizate cylinder for acoustic pipe testing, 50 mm in diameter, 100 mm in height, was made by a vulcanization process of 150 °C × 30 min as well.

Dynamic mechanical thermal analyses (DMTAs) [15]

All of the tanδ–T curves were tested by DMTA (DMTA-V Rheometric Scientific). 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 °C/min, the frequency was 10 Hz, and the range of testing temperature was from -100 to 100 °C.

Wide angle X-ray diffraction (WAXD) [16]

The crystalline structure of EU gum and its blends were tested by WAXD (WAXD-D/max2500 Rigaku). The rectangle test-pieces were cut from the vulcanizate sheet of various rubbers with 15 mm in length, 15 mm in width, and 1.5 mm in thickness. Cu (Kα1), $\lambda = 1.54056$ Å, $5° < 2\theta < 30°$, scan rate 3°/min.

Differential scanning calorimetry (DSC) [17]

The melting points of EU gum and its blends were tested by DSC (DSC1 Mettler-Toledo). The range of tested temperature was from -10 °C to 100 by 10 °C/min of heating rate.

Acoustic pipe [18]

The sound absorption coefficient (SAC) of EU gum and its blends were tested by acoustic pipe, air backing pattern is adopted, the test is carried out under ambient temperature, and the water temperature is 25 ± 5 °C.

Result and discussion

Damping properties of EU gum, NR, CR, and CIIR

The envelop area under the tanδ curve of rubber material is used to characterize their damping properties [7], the bigger the envelop area, the better the damping property. As shown in Fig. 1, in terms of the envelop area at T_g zone, the damping property of CIIR is the best, the damping properties of CR and NR are better, and the damping property of EU gum is poor. However, it is different from conventional

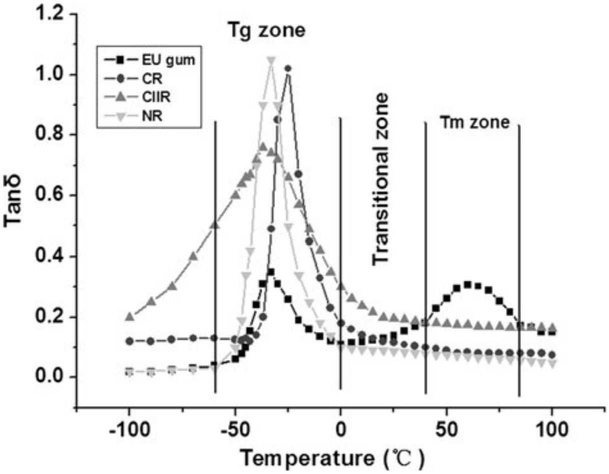


Fig. 1 Tanδ–T curves of four different rubbers

rubbers that have only one T_g damping zone, EU gum has three damping zones which are T_g zone, T_m zone, and their transitional zone, respectively. The damping property of EU gum is poor at T_g damping zone, but it is good at transitional damping zone and great at its T_m damping zone.

In general, the damping properties of conventional rubber materials are great at low temperature for their lower glass transitional temperatures ($T_g \ll 0$ °C). However, most of the damping materials need to be applied under ambient temperature (0–40 °C) or higher temperature. So their great damping properties can not be used effectively under ambient temperature or higher temperature which is just at the transitional damping zone and T_m damping zone of EU gum. As shown in Fig. 2, the tanδ–T curves of EU gum at ambient temperature are compared with that of NR, CR, and CIIR.

It is seen from Fig. 2 that the tanδ–T curves of NR, CR, and CIIR at ambient temperature decrease with the increase in temperature. However, the tanδ–T curve of EU gum will increase with rising of temperature. Its tanδ value exceeds that of NR when $T = 0$ °C, and exceeds that of CR when $T = 18$ °C, and close to that of CIIR when $T = 40$ °C.

Under-water sound absorption properties of EU gum, NR, CR, and CIIR

Sound absorption coefficient (α) is used to characterize the under-water sound absorption properties of materials [1]. The bigger the SAC value, the better the sound absorption property, vice versa. The SAC values of four rubbers mentioned above at ambient temperature are plotted against different sound frequencies in Fig. 3. As shown in Fig. 3, all the SAC–F curves of rubber materials increase first, decrease with sound frequency rise, and then form a flat peak at 6–14 kHz. And their SAC–F curves will increase again at high sound frequency region ($F > 18$ kHz). It indicates that rubber material is only sensitive to some frequency

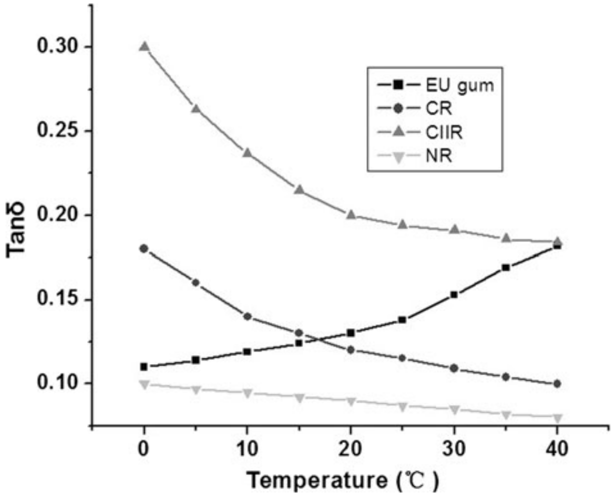
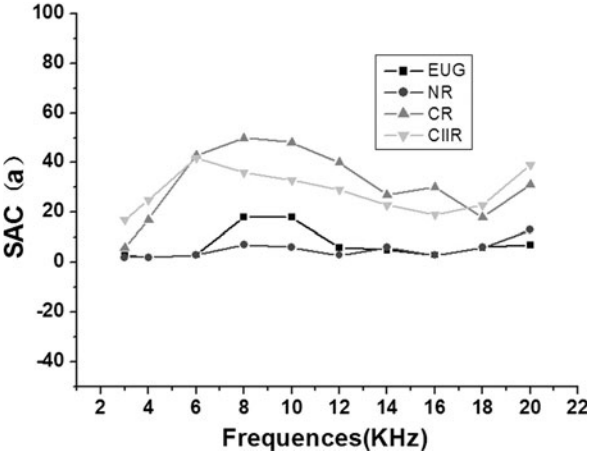


Fig. 2 Tanδ–T curves of four different rubbers at ambient temperature

Fig. 3 SAC–F curves of four different rubbers



band of sound absorption. Whatever, their SAC values are all very small at low frequency band, such as $F = 3$ kHz.

It is seen from Fig. 3, the SAC values of CR and CIIR are far bigger than those of EU gum and NR, and the SAC values of EU gum are bigger than those of NR as well. Such results are basically in agreement with their tanδ values, namely, the bigger the tanδ value, the higher the SAC value, vice versa. However, the SAC values of rubber materials are not accordance with their tanδ values entirely. As shown in Fig. 2, the tanδ values of CIIR are larger than those of CR at 0–40 °C, but their SAC values are almost equal, and the SAC values of CR are even larger than those of CIIR at frequency band of 6–18 kHz. Furthermore, the tanδ values of EU gum exceed those of CR at 18 °C, but the SAC values of EU gum are far lower than those of CR. It indicates that there must be other factors which can affect SAC except damping property of rubber.

In addition, on the whole frequency band, all the SAC values of EU gum and NR are very small which basically belong to sound transparent material or sound insulation material. And the SAC values of CR and CIIR are almost less than 50% except some frequency and can not meet the request of sound absorption material.

Damping properties of EU gum blends with CR and CIIR

In terms of blending ratio: EU gum/CR (CIIR) (80/20, 50/50, and 20/80), together with EU gum and CR (CIIR), their tanδ–T curves are shown in Figs. 4 and 5. It is seen from the two pictures that mixing EU gum into CR or CIIR will reduce their damping properties at T_g zones, but will increase their damping properties at medium–high temperature (40–80 °C). The reason is that the crystallization of EU gum will reduce their tanδ values at T_g zone, and increase their tanδ values at T_m zone. In addition, we can find that the tanδ–T curves of EU gum/CIIR blends have two damping peaks which are T_g peak and T_m peak, respectively. However, the tanδ–T curves of EU gum/CR blends have three damping peaks which are T_g peak of EU gum, T_g peak of CR, and T_m peak of EU gum, respectively. It indicates that the compatibility of EU gum and CIIR is better than that of EU gum and CR.

At ambient temperature (0–40 °C), EU gum is just at its transitional damping zone. However, it is not obvious for EU gum to improve the damping properties of CR or CIIR. As shown in Figs. 6 and 7, the tanδ–T curve of EU gum is increased; the tanδ–T curves of CR or CIIR are decreased with the increase in temperature rise. For CR/EU gum blends, their tanδ–T curves are as the same magnitude as that of CR; for CIIR/EU gum blends, their tanδ–T curves are lower than that of CIIR.

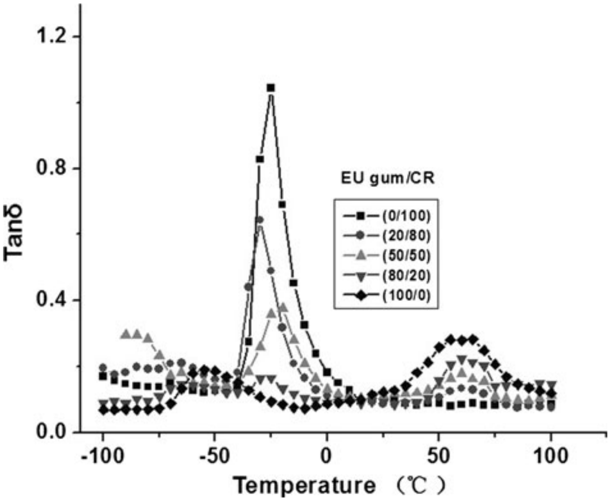


Fig. 4 Tanδ–T curves of CR and its blends with EU gum

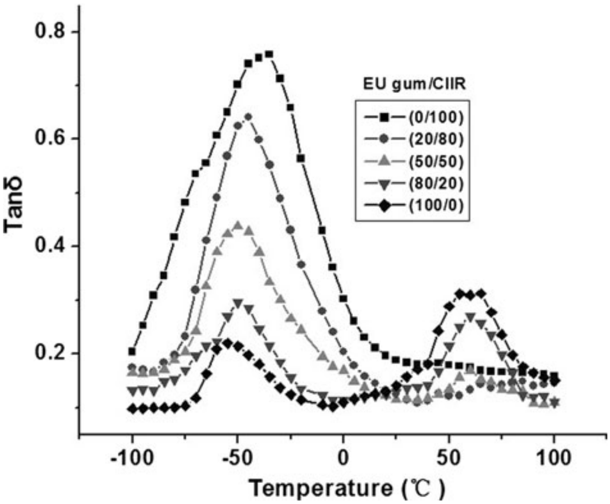


Fig. 5 Tan*δ*–*T* curves of CIIR and its blends with EU gum

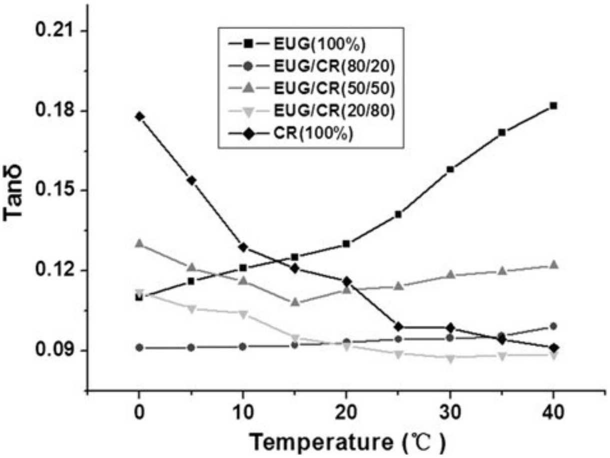


Fig. 6 Tan*δ*–*T* curves of CR and its blends with EU gum at ambient temperature

Under-water sound absorption properties of EU gum blends with CR and CIIR

In terms of blending ratio: EU gum/CR (20/80, 40/60, 60/40, and 80/20), together with EU gum and CR, their SAC–*F* curves are plotted in Fig. 8. It is seen from Fig. 8, the SAC values of blends will increase greatly compared with CR if EU gum is less than 50%, their SAC values even exceed 90% at some frequency bands. However, the SAC values of blends are as poor as that of EU gum if EU gum is more than 50%. So a conclusion can be drawn: for EU gum/CR blends, a critical value of blend ratio of EU gum must exists which is equal to 50%. In addition, all the SAC values of EU gum/CR (40/60) blend are high from low frequency to high

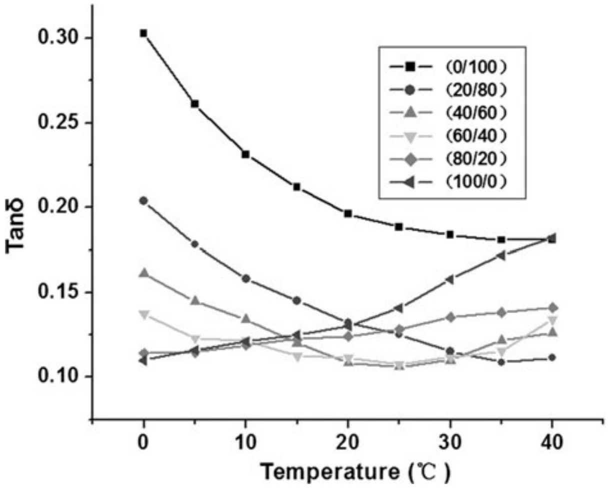


Fig. 7 Tanδ–T curves of CIIR and its blends with EU gum at ambient temperature

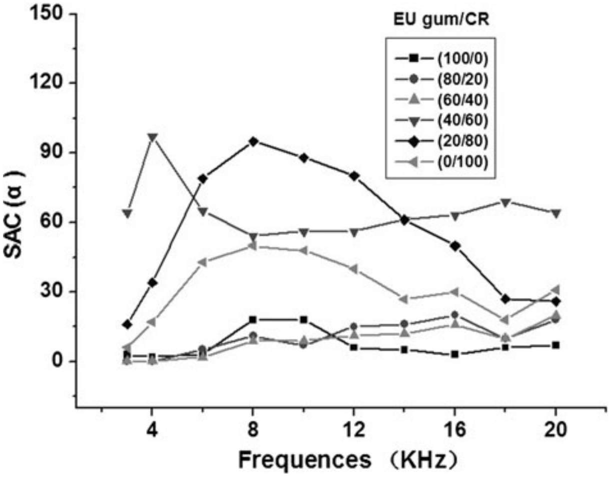


Fig. 8 SAC–F curves of CR and its blends with EU gum

frequency, which indicates that mixing a certain amount of EU gum into CR can greatly broaden their under-water sound absorption frequency band.

For CIIR, the additive amount of EU gum is controlled within 50%. Their SAC values are plotted against sound frequency in Fig. 9. It is seen from Fig. 9, except the EU gum/CR (50/50) blend, all the SAC–F curves of EU gum/CIIR blends are far higher than that of CIIR. It confirms again, for EU gum/CIIR blends, a critical value of the additive amount of EU gum exists which is equal to 50%. If EU gum >50%, their under-water sound absorption properties are great, if EU gum <50%, their under-water sound absorption properties are very poor.

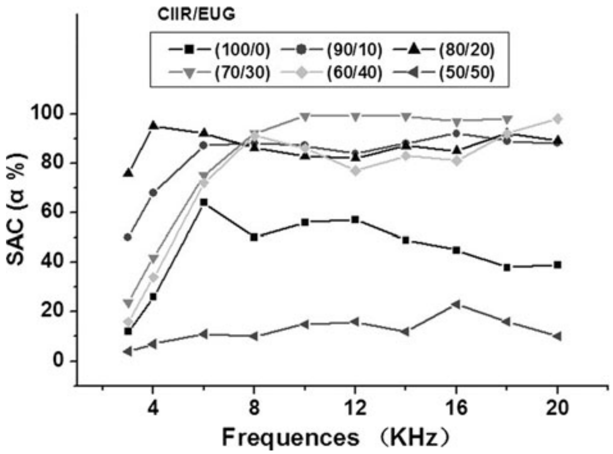


Fig. 9 SAC–F curves of CIIR and its blends with EU gum

In addition, all the SAC–F curves of EU gum blends (EU gum $< 50\%$) will increase first with frequency rise, then keep a constant value (90% or so) when the frequency is over 8 kHz. At low frequency region ($F < 6$ kHz), the SAC value of blends will increase gradually with decrease in the EU gum. For example, at 3 kHz, the SAC value of EU gum/CIIR (40/60) blend is 16%, EU gum/CIIR (30/70) blend is 24%, and EU gum/CIIR (20/80) blend is 76%. Especially, the SAC values of EU gum/CIIR (20/80) blend almost keep 90% over all of the sound frequencies tested. It confirms again, like CR, EU gum can widen the acoustic absorptivity of CIIR, especially it greatly increase its low frequency acoustic absorptivity at 3 kHz.

Analysis on the mechanisms of under-water sound absorption properties of EU gum blends

Relaxation absorption of rubber materials

As discussed above, the additive amount of EU gum has a critical point which is equal to 50%. Less than 50%, the main body of the blends is still damping rubber, such as CR and CIIR. So the relaxation absorption of damping rubber is still the base of the under-water sound absorption property of EU gum blends. The average SAC values of CR and CIIR are 31 and 28.6%, respectively, which are calculated from Fig. 2 over all the sound frequency tested. So the contribution of relaxation absorption of rubber material to EU gum blend is about 30%.

Spacial diffuse reflection absorption of EU gum crystallite

The EU gum is a natural polymer which can crystallize under ambient temperature [19–23]. It will also crystallize under the condition of vulcanization if its cross-link density does not exceed Yan's point [8, 9]. Take EU gum/CIIR blends for example, the crystalline structure of EU gum/CIIR blends are tested by WAXD, as shown in

Fig. 10 WAXD curves of EU gum/CIIR blends. (*a*) EU gum100%, (*b*) EU gum80%, (*c*) EU gum60%, (*d*) EU gum40%, (*e*) EU gum20%, and (*f*) CIIR100%

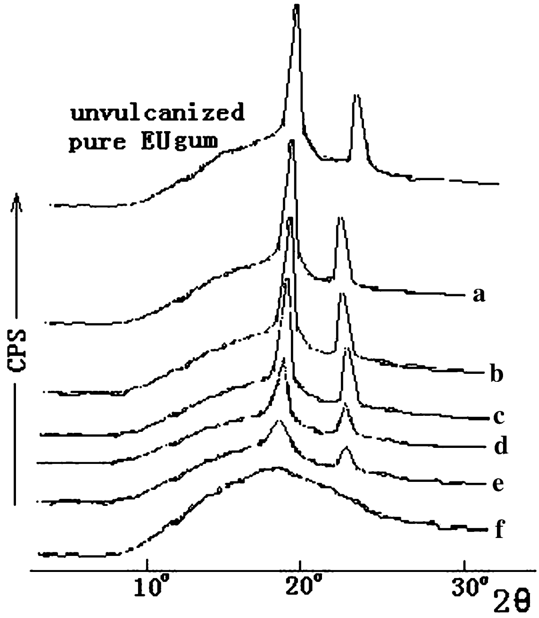


Fig. 10, the unvulcanized EU gum has two main response peaks, one is at $2\theta = 18.7°$, and the other is at $2\theta = 22.7°$. Vulcanization does not change the position of the two response peaks of EU gum, but will decrease their peak height, see spectrum a in Fig. 10. Blending EU gum into CIIR does not also change the position of the two response peaks, but will also decrease their peak height, see spectra b, c, d, and e in Fig. 10. It indicates that vulcanization or blending can not change the crystalline form of EU gum.

The melting points of EU gum/CIIR blends are tested by DSC, as shown in Fig. 11; EU gum has two melting peaks: one is at 56 °C and the other is at 64 °C. Vulcanization can decrease the T_m of EU gum, see curve a in Fig. 11, the melting points of the vulcanized EU gum are 42 and 54 °C, respectively. Blending CIIR into EU gum can also decrease the T_ms of EU gum/CIIR blends, see curves b, c, d, and e in Fig. 9.

From the analysis discussed by WAXD and DSC, a conclusion can be drawn: blending EU gum into CIIR can form two phase structure, one is amorphous phase of rubber (including CIIR and amorphous EU gum) and the other is crystalline phase of EU gum. The sound velocity of rubber is far different from that of crystal of EU gum which will mismatch their acoustics impedances. So the crystal of EU gum in the rubber matrix will reflect incident sound wave, as shown in Fig. 12. This is also the reason why the under-water sound absorption property of EU gum is very poor.

If EU gum is more than 50%, the main body of the blend is EU gum, and the size of crystal of EU gum is still large, like EU gum, it can reflect most incident sound

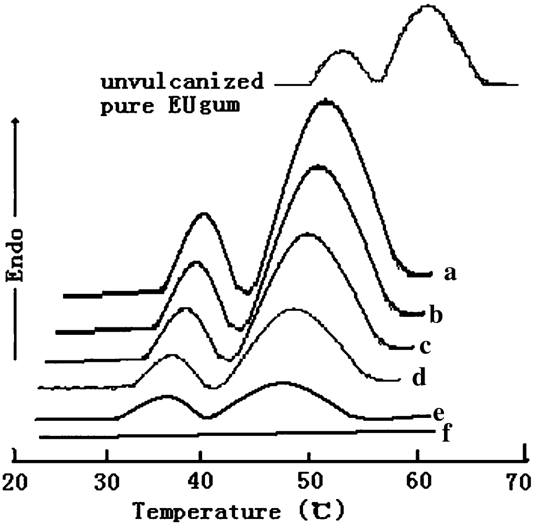


Fig. 11 DSC curves of EU gum/CIIR blends. (*a*) EU gum100%, (*b*) EU gum80%, (*c*) EU gum60%, (*d*) EU gum40%, (*e*) EU gum20%, and (*f*) CIIR100%

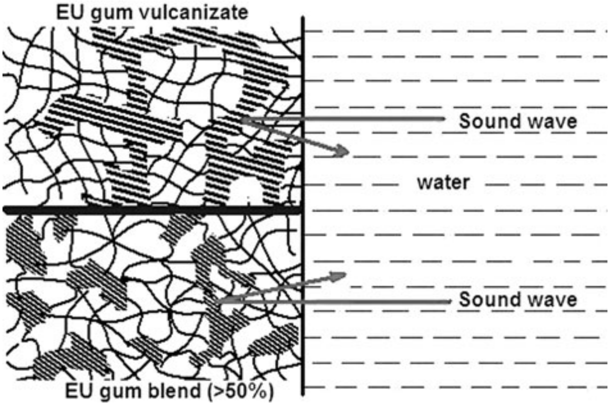


Fig. 12 Diagram of transmission of sound wave in EU gum and its blends (*up*: EU gum; *down*: EU gum blends (EU gum > 50%))

wave, as shown in Fig. 12. So their under-water sound absorption properties are very poor too.

If EU gum is less than 50%, the crystal of EU gum is broken into many microcrystals scattering in the continuous rubber matrix, like many islands in the sea. The rubber matrix is continuous phase, and the microcrystal of EU gum is dispersed phase. The acoustics impedance of rubber matrix matches that of water very well, so the incident sound wave can enter into the rubber matrix easily and almost no sound wave reflections occur; the acoustics impedance of the microcrystal of EU gum mismatches that of water, so sound wave reflection will happen when the incident sound wave meets microcrystal of EU gum. There are so many

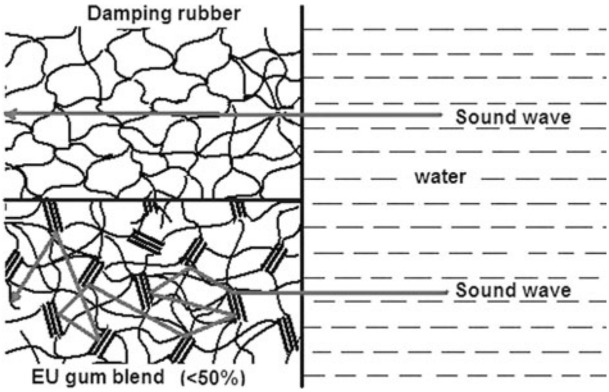


Fig. 13 Diagram of transmission of sound wave in damping rubber and EU gum blends (*up*: Damping rubber; *down*: EU gum blends (EU gum < 50%))

microcrystals of EU gum in the rubber matrix, so the incident sound wave can be reflected more times, as shown in Fig. 13. And this phenomenon will greatly increase the travel path of incident sound wave which will dissipate much sound energy. The nature of the special diffuse reflection absorption is still the relaxation absorption of damping rubber.

Shear deformation absorption of the interface between crystalline hard phase and rubber soft phase

In the two phase structure of EU gum blends, the crystalline structure of EU gum is hard phase, and the rubber network structure is soft phase. If the additive amount of EU gum is less than 50%, as discussed above, the crystal of EU gum is broken into many microcrystals scattering in the rubber network. The soft rubber network is continuous phase, and the hard microcrystal of EU gum is dispersed phase. When a beam of sound wave is launched on the surface of the test-piece of EU gum blend, the sound pressure will compress the test-piece, and the volume deformation occurs. The rubber network is soft phase, and deforms largely, and the microcrystal of EU gum is hard phase, and deforms little. So the volume deformation will transform into shear deformation in the interface between soft phase and hard phase, as shown in Fig. 14. In addition, cross-linked bonds strengthen the connection of microcrystal hard phase and rubber network soft phase which can increase shear deformation. Shear deformation can dissipate much more sound energy than that of volume deformation. And there are so many microcrystals in the EU gum blend, and the total surface of all the microcrystals must be very large, so their under-water sound absorption properties increase greatly.

If EU gum >50%, the main body of blends is still EU gum, the size of crystal of EU gum is still very large, and their total surface must be far smaller than those of microcrystals, so the contribution of shear deformation absorption is limited to under-water sound absorption property.

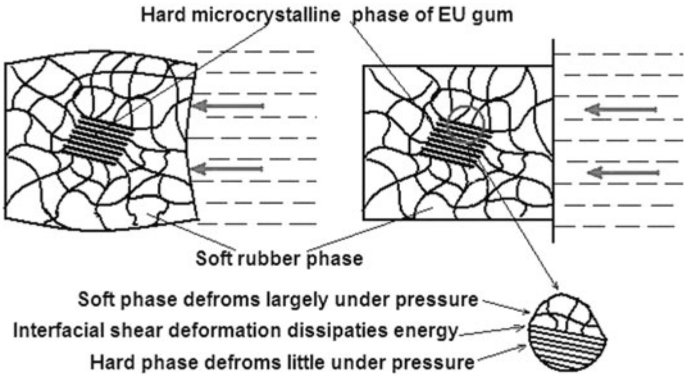


Fig. 14 Diagram of shear deformation in the interface between soft and hard phase

Reducing crosslinking degree can increase under-water sound absorption property

Crosslinking degree has great influence on the under-water sound absorption property of rubber materials. Take EU gum/CIIR (10/90) for example, the additive amount of crosslinking agent is cut in half, and their SAC values are plotted against sound frequency in Fig. 15. As shown in Fig. 15, at high crosslinking degree, the SAC–F curves increase first, decrease with sound frequency increase, and then form a plateau in the frequency range 8–16 kHz. At low crosslinking degree, the SAC–F curves increase first with the sound frequency increase, then reach a constant when $F > 8$ kHz. Both their SAC values at the frequency range 8–16 kHz are very high (90% or so) which confirms again that blending a certain amount of EU gum into CIIR can greatly increase their under-water absorption properties. However, the

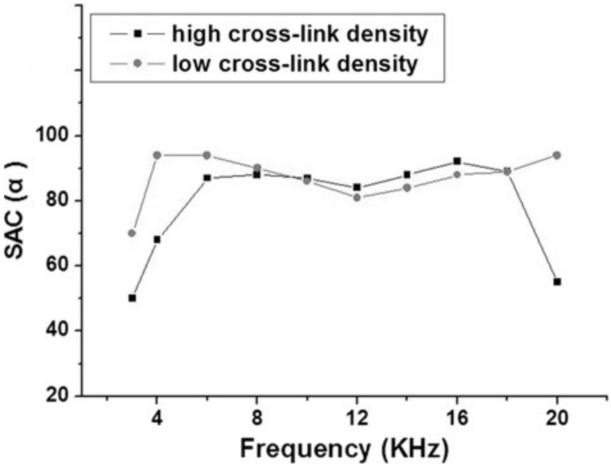


Fig. 15 SAC–F curves of EU gum/CIIR (10/90) blends in different crosslinking degrees

SAC values of low crosslinking degree at low frequency region ($F < 8$ kHz) and high frequency region ($F > 16$ kHz) are greatly increased comparing with that of high crosslinking degree. It indicates that reducing crosslinking degree will especially increase the SAC values at low frequency ($F < 8$ kHz) and high frequency ($F = 20$ kHz) and can effectively expand the under-water sound absorption property to full frequency.

Conclusion

Unlike the conventional rubber materials whose acoustic impedances match that of water very well, the acoustic impedance of EU gum mismatches that of water. As a result, the sound wave can enter into conventional damping rubber easily, such as CR and CIIR, but will be reflected by EU gum. So blending a certain amount EU gum into CR and CIIR as microcrystal to reflect sound wave more times can effectively improve the under-water sound absorption property of conventional damping rubber. In addition, reducing crosslinking degree can effectively expand their under-water sound absorption properties to full frequency.

Acknowledgment This research was supported by grants from the early pre-research of the major basic special research of the Ministry of Science of China (Grant No. 2002CCA03600).

References

1. Wang RJ (1983) Manual of underwater acoustical materials (in Chinese). Science Press, Beijing, p 1
2. 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 63
3. Ma DY (1983) Acoustics handbook (in Chinese). Science Press, Beijing, p 350
4. Zhong AS (2001) Low-frequency acoustic properties of the rubber material and structural with pressure resistance. Prod Technol (in Chinese) 2:21
5. Zhang HJ, Qiu BH, Shi L, He P (2001) Current status and development trend of the anechoic tiles technology. Ship Sci Technol (in Chinese) 4:7
6. Du HG, Zhu ZM, Gong XF (2001) Basic of acoustics (in Chinese), 2nd edn. Nanjing university press, Nanjing, p 452
7. He MJ, Chen WX, Dong XX (2000) The physics of polymer (in Chinese). Fudan University Press, Shanghai, p 343
8. Yan RF (1996) Polymeric materials encyclopedia. In: Salamone JC (ed) Eucommia ulmoide gum. vol 3. CRC Press, Boca Raton, p 2291
9. Qian RY, Wu ZC, Xue ZH, Yan RF (1995) Length of chain segment motion needed for crystallization. Macromol Rapid Commun 16:19–22
10. Boochathum P, Chiewnawin S (2001) Vulcanization of cis- and trans-polyisoprene and their blends: crystallization characteristics and properties. Eur Polym J 37(3):429
11. 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
12. 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
13. 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

14. Xie SZ, Liu DX, Zhou ML (1993) Handbook of rubber industry (in Chinese), 2nd edn. Chemistry Industry Press, Beijing, p 317
15. Guo ML (2002) Dynamic mechanical thermal analysis of polymer and composite materials (in Chinese). Chemical Industry Press, Beijing, p 20
16. Wu G (2001) The application and characterization of material structure (in Chinese). Chemistry Industry Press, Beijing, p 209
17. Wu G (2001) The application and characterization of material structure (in Chinese). Chemistry Industry Press, Beijing, p 423
18. Liu HW, Yao L, Xue ZH, Zhang JC (2006) A mixed method for measuring low-frequency acoustic properties of macromolecular materials. Sci China Ser G Phys Mech Astron 49(6):729
19. Cooper W, Vaughan G (1963) Melting transitions in diene polymers. J Polym Sci A 1:159
20. Mandelkern L, Quinn F Jr, Roberts AD (1956) Thermodynamics of crystallization in high polymers: gutta percha. J Am Chem Soc 78(5):926
21. Kuo CC, Woodword AE (1982) Crystallization of trans-1,4-polyisoprene. J Polym Sci Polym Phys Ed 20(9):1669
22. Anandakumaran K (1983) Noncrystalline component in dilute-solution-grown crystals of trans-1,4-polyisoprene. Macromolecules 16:563
23. 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