

Study on the Damping Mechanism of Chlorinated Butyl Rubber/C5 Petroleum Resin Composites by Experimental and Molecular Dynamics Simulation

C Yin, J Zhu, L Lu, M F Wang, Q Zhang and S Z Wu*

College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

Corresponding author and e-mail: S Z Wu, wusz@mail.buct.edu.cn

Abstract. In this work, the damping mechanism of C5 petroleum resin/chlorinated butyl rubber (CIIR) composites were studied by combining experimental and molecular dynamics (MD) simulation. From a macro perspective, the damping parameters (glass transition temperature T_g and effective damping temperature region ΔT) and the activation energy (E_a) were obtained by dynamic mechanical thermal analysis. In the micro level, four intermolecular interaction parameters (binding energy $E_{binding}$, fractional free volume, mean square radius of gyration and mean square displacement) were calculated by molecular dynamics simulations. These studies are expected to provide the useful information in understanding the damping mechanism and to offer the theoretical guidance for optimizing the damping properties of polymer composites.

1. Introduction

In the past decades, how to effectively reduce the noise pollution or mechanical vibration has become a hot topic[1]. Viscoelastic polymer used as damping materials have attracted a considerable attention for converting vibration or noise energy to heat energy. As we know, the excellent damping materials should have suitable glass transition temperature which is better close to application condition and also should be with the wide effective damping temperature region.

Comparing with other polymer matrices, the chlorinated butyl rubber (CIIR) has preferable damping properties due to its dense side methyl groups, lower molecular mobility and higher energy loss. According to reports in the literature[2], CIIR shows a unique relaxation behavior which are the asymmetrical double-peak structure with a maximum on the high temperature side and the additional shoulder on the low temperature side. Plazek [3] and Huang[4, 5] examined that different modes of CIIR molecular motion contribute to the transition region from local segmental motion, sub-Rouse mode, and Rouse mode. However, the loss peaks of the above three modes of CIIR molecular motion are located at lower temperature region rather than room temperature. Therefore, in order to broad the effect damping temperature region of CIIR composites, many ways have been attempted such as blend modification, copolymerization, gradient polymers, interpenetration network (IPN) polymers etc[6].

Hindered phenols or hindered amines [6] often be used to improve the damping properties of composites. For example, Yang [7] investigated that hindered phenol AO-80 effectively improved the damping performance of hindered phenol/polyacrylate hybrids. However, the method of modifying with small polar molecules also has many shortcomings, such as the easy migration of small molecule [8], which makes the loss factor $\tan \delta$ decrease, and consequently the damping properties of composites fall off. Meanwhile hindered phenols are also relatively expensive. Such as the price of C5 petroleum resin (Puyang Ruisen Petroleum Resin Factory (China)), which can also effectively improve the damping properties, is just 3.9 dollar per kilogram in 2017 for reducing the costs drastically. The C5 petroleum resin is a kinds of amorphous polymers with low molecular weight (from 300 to 3000) and the glass transition temperature region is located near the room temperature which shows the capacity to improve the damping performance of rubber composites in practical application. Wu and co-workers investigated the CIIR/C5 petroleum resin composites with different contents, the glass transition temperature increased and the effective damping temperature range was successfully broadened[9,10]. However, the mechanisms for improving the damping performance is not very clear, some microscopic parameters (such as the interactions and mobility of the molecular chains) cannot be obtained. With the development of computational technology, the molecular simulation has provided an effective tool to figure out the microstructural and the properties of materials at a molecular level. Therefore, in this work the molecular dynamics simulation is introduced to study the damping mechanism of C5 petroleum resin/CIIR composites.

2. Simulation results and analysis

The construction procedure of the C5 petroleum resin/CIIR composites cells is shown in Figure 1. The chlorinated isoprene repeat unit, isobutylene repeat unit and isoprene repeat unit were first randomly copolymerized as a CIIR polymer chain. Subsequently, 500 ps of NVT simulation was performed at 298 K and 1000 ps of NPT simulation is performed at 0.1MPa pressure to further relax the polymer chain structure.

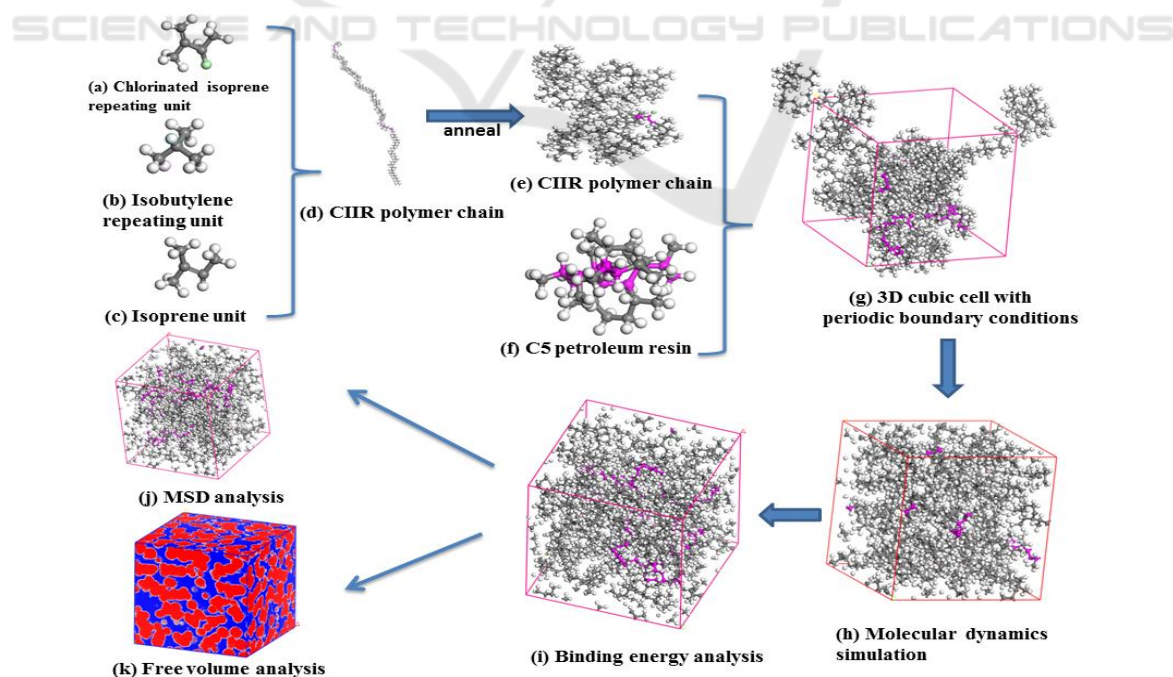


Figure 1. Construction procedures of C5 petroleum resin/CIIR systems for MD simulation.

The binding energy ($E_{binding}$) is introduced to investigate the influence of intermolecular interaction on damping properties. Table 1 shows that with increasing content of C5 petroleum resin, $E_{binding}$ increases gradually, which indicates that the intermolecular interactions between CIIR and C5 petroleum resin are constantly increased. Meanwhile, the binding energy is always kept the positive value which indicates good compatibility in the C5 petroleum resin/CIIR system [11].

Table 1. Binding energy with different C5 petroleum resin contents.

Mass ratio of C5 petroleum resin/CIIR	E_{total} (kcal mol ⁻¹)	$E_{C5 \text{ petroleum resin}}$ (kcal mol ⁻¹)	E_{CIIR} (kcal mol ⁻¹)	$E_{binding}$ (kcal mol ⁻¹)
0/100	443.010	0	443.010	0
10/100	-702.808	52.718	-616.450	139.116
20/100	-1290.370	61.386	-1147.060	204.696
30/100	-766.773	90.170	-576.742	280.160
40/100	-1285.420	136.328	-1052.340	369.408
50/100	-1345.920	137.939	-1042.420	441.438

The fractional free volume (FFV) [11] may be used to reflect the efficiency of chain packing in C5 petroleum resin/CIIR systems which the results are shown in Figure 2. With increasing content of C5 petroleum resin, the FFV decreases since the stronger intermolecular interaction causes close packing of molecular chains, shortens the interspace and increases the friction between the molecular chains, which is resulted the enhanced damping performance.

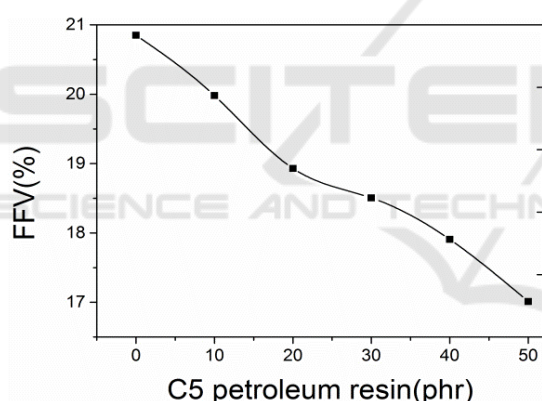


Figure 2. The fractional free volume (FFV) of C5 petroleum resin/CIIR composites with different C5 petroleum resin content.

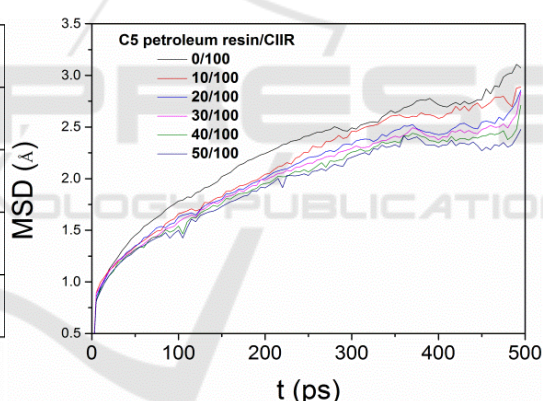


Figure 3. The mean square displacement (MSD) of CIIR chains with different C5 petroleum resin content.

The mean square displacement (MSD) may be used to describe the activities of the molecular chain [12]. Figure 3 was the simulation result of MSD . With the increase of C5 petroleum resin content, the MSD of CIIR chains gradually decreases, which means the movement of CIIR chains becomes more difficult, and the glass transition temperature (T_g) of C5 petroleum resin/CIIR systems should move towards high temperature direction.

The radius of gyration is a parameter commonly used to describe the size of a random polymer chain. The polymer chain is more flexible with smaller R_g [13]. Figure 4 shows that the mean square radius of gyration of CIIR chains with different C5 petroleum resin content. It was noted that as the content of C5 petroleum resin increases, the mean square radius of gyration of CIIR chains gradually enhances. This is because with the increase of C5 petroleum resin content, the intermolecular

interaction between C5 petroleum resin and CIIR gradually increases and there are good compatibility between these two, which the CIIR chains becomes more stretched resulting in increasing values of the mean square rotation of CIIR chains and the activity of the CIIR chains falls off. This result is consistent with the previous *MSD* effects.

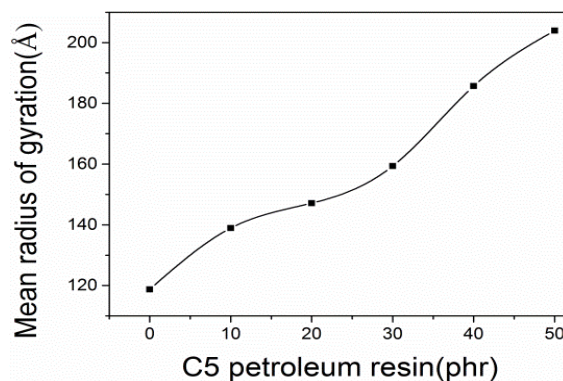


Figure 4. The mean square radius of gyration of CIIR chains with different C5 petroleum resin content.

3. 3. Experiments and results

3.1.1. Materials and sample preparation. The chlorinated butyl rubber (CIIR, product code: 1066) with a chlorination concentration of 1.2% is purchased from Japan Synthetic Rubber Co. (Japan). The C5 petroleum resin is from Puyang Ruisen Petroleum Resin Factory (China). The composites were prepared according to the following procedures: (1) the CIIR matrix was first plasticized on a $\Phi 152.4$ mm two-roll mill at room temperature for 4 min. Then the C5 petroleum resin was added to CIIR with mass ratio of 0/100, 10/100, 20/100, 30/100, 40/100, 50/100 respectively, which is as same as the mass ratio to build the amorphous cell in MD simulations. (2) the blends were mixed on a two-roll mill at room temperature for 5min with compounding and crosslinking additives (including 5.0 phr of zinc oxide, 1.0 phr of stearic acid, 1.5 phr of tetramethylthiuram disulfide, 3 phr of 2,2'-dibenzothiazole disulfide and 2.0 phr of sulfur). (3) the composites were hot-pressed and vulcanized at 160 °C under the pressure of 15 MPa and then make the samples cool down to room temperature.

3.1.2. DMA analysis of C5 petroleum resin/CIIR composites. The damping properties and the changes of molecular dynamics of polymer of C5 petroleum resin/CIIR have been studied by DMA experiments [14]. The damping performance is shown in Figure 5(a). It shows that the T_g and ΔT increase gradually with increasing C5 petroleum resin content. Generally, the T_g values of CIIR can be extracted from the peak temperatures in the $\tan \delta$ curves. But it is found that the $\tan \delta$ curve of CIIR displays an asymmetrical peak with a shoulder peak at about -38 °C and a maximum peak at -22 °C. According to reports in the literature [15], $\tan \delta$ curve may be divided into three peaks which can be correspond to the local segmental, sub-Rouse mode and Rouse mode peaks respectively. The local segmental, which is a cooperative motion of neighboring chains each involve several repeat units, is the enthalpic and related with the glass transition temperature. Meanwhile the Rouse mode, which is based on the motions of Gaussian sub-molecules formed by sufficient number of repeat units in each chain, is entropic in nature. As Figure 5 shows that both the maximum and the shoulder of the $\tan \delta$ peak of CIIR move to the higher temperature with the increase of C5 petroleum resin content, which indicating C5 petroleum resin limits the space for CIIR due to intermolecular interaction between C5 petroleum resin and CIIR. Meanwhile, it is noted that C5 petroleum resin

limits these two relaxation modes (local segmental motion and Rouse modes relaxation) to different extents.

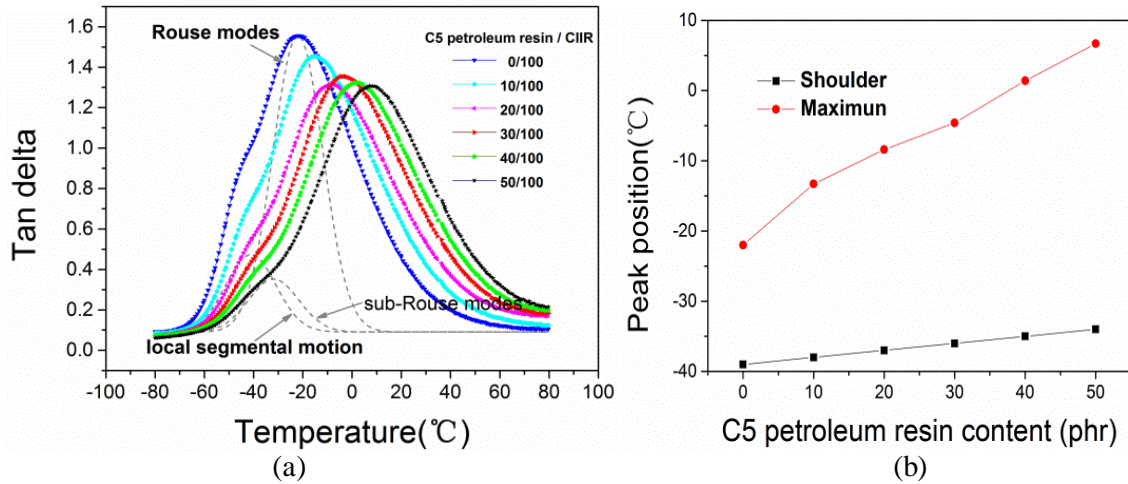


Figure 5.(a) Temperature dependence of loss factor ($\tan\delta$) for C5 petroleum resin/CIIR composites, and (b) Peak position of different modes of C5 petroleum resin/CIIR composites with different C5 petroleum resin content.

The activation energy (E_a) is introduced to quantify the internal friction. According to the storage modulus (E')–temperature curves presented in Figure 6 (a), E_a can be calculated through the following Arrhenius-type equation [16]:

$$\frac{E'}{E_0} = \exp\left[\left(\frac{E_a}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (1)$$

Where E' is the storage modulus at temperature T , E_0 is the storage modulus at reference temperature T_0 and R is the universal gas constant. Based on Eqn (1), the logarithm of the storage modulus is almost linear with the inverse temperature, which the result is shown in Figure 6 (b). It can be seen that the E_a is almost proportional to the slope of the straight line. For the 50/100 system, the deviation occurs at a low temperature which may be owed to aggregations of the C5 petroleum resin. Table 2 listed the results of the E_a , showing that E_a of CIIR chains increase gradually with increasing C5 petroleum resin content. It indicates that more energy is required to overcome internal friction of CIIR chains, which is consistent with the result of MSD .

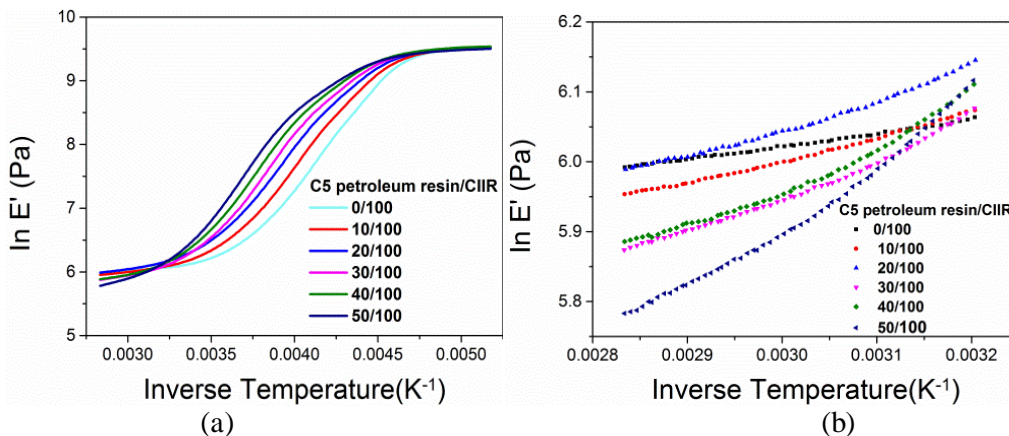


Figure 6.(a) Storage modulus in temperature sweep for C5 petroleum resin/CIIR composites, and (b) logarithm of storage modulus against inverse temperature for C5 petroleum resin/CIIR composites.

Table 2. Damping properties of CIIR and C5 petroleum resin/CIIR composites

Mass ratios of C5 petroleum resin/CIIR	tan δ_{\max}			tan $\delta > 0.3$			
	Value	T_g (°C)		T_1^a (°C)	T_2^a (°C)	ΔT^a (°C)	E_a (kJ mol ⁻¹)
0/100	1.56	-22.00		-57.70	29.45	87.15	1.53
10/100	1.45	-13.30		-54.10	38.25	92.35	2.70
20/100	1.31	-8.40		-50.35	45.60	95.95	3.38
30/100	1.35	-4.60		-45.35	52.10	97.45	4.32
40/100	1.32	1.40		-44.50	56.45	100.95	4.86
50/100	1.31	6.70		-39.45	62.40	101.85	7.27

a. T_1 , T_2 is the starting and ending temperatures with the loss factor $\tan\delta \geq 0.3$ range. ΔT is the difference value from T_1 to T_2 .

4. Conclusions

The damping mechanism of C5 petroleum resin/CIIR composites was studied by combining experimental and molecular dynamic simulations. With the increase of C5 petroleum resin content, the damping parameters (T_g and ΔT) gradually increase, which shows C5 petroleum resin improve the damping performances of the composites. As the two relaxation processes need different free volume, the local segmental motion and Rouse mode have different responses to the space limited from DMA experiments. The simulation parameters (FFV , MSD) are getting smaller, which shows the C5 petroleum resin plays a key role like anti-plasticizer in decreasing the free volume fraction of the blends. The presence of C5 petroleum resin slightly confines the molecular mobility of the local segmental motion of CIIR, but greatly confines the molecular mobility of Rouse mode of CIIR.

Acknowledgements

The authors acknowledge the National Natural Science Foundation of China (Grant No. 51473012).

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