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ORIGINAL PAPER

Evolution of Payne effect of silica-filled natural rubber in curing process

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Abstract

Vulcanisation is the key process for determining the final properties of elastomers due to the relationship between curing condition and viscoelastic behaviour. This study focuses on the variations in the dynamic behaviour of silica-filled natural rubber caused by crosslinking. The rubber samples with different degrees of curing (DOC) are prepared by thermal quenching during the crosslinking process. The strain sweep mode is used to study the Payne effect. The Kraus model is used to fit the test data. The relationship between the parameters of Kraus model and DOC is obtained at small strain ($<10\%$). The storage modulus at small strain amplitudes (usually $<0.01\%$) G'_0 is proportional to DOC; however, the storage modulus at large strain amplitudes G'_∞ has small changes with DOC. The characteristic value of the strain amplitude γ_C shifts to large strain and the maximum loss modulus G''_m decreases with the increase of DOC. In addition, a deviation between Kraus model and experiment is observed when the strain is larger than 10%, and the loss modulus increases with the increase of strain amplitude. The deviation decreases when DOC increases. The mechanism for this deviation is discussed and the interaction between silica filler and rubber chain might be responsible for the observed deviation.

Keywords Silica-filled nature rubber · Payne effect · Vulcanisation · Crosslink density

Introduction

Filled rubber is one of the most important elastomers widely used in many engineering fields such as civil engineering, mechanical engineering, automobile engineering, and aerospace engineering due to their high elasticity, high damping, and larger elongation at failure. These excellent characters can only be acquired by the curing process which is a chemical process that crosslinks the linear rubber chain molecules. Vulcanisation is the key process that affects the viscoelastic behaviour of filled rubber. However, the relationships between curing conditions and mechanical behaviour are still unclear. Silica filler can obviously decrease the loss modulus of filled rubber compared to carbon black filler. The mechanisms of the effects of refined silica filler on vulcanised rubber are widely studied, because the interaction between filler and rubber chains can be enhanced with the assistance of silane coupling agent such as TESPT [1]. Therefore, the loss modulus of silica-filled rubber is lower than that of carbon black filled rubber. Silica-filled rubber as an important raw material for green tires can decrease rolling resistance significantly.

The complex mechanical behaviour of filled rubbers, such as hyper-elasticity [2, 3], viscoelasticity [4–6], Mullins effect [7], and Payne effect [8, 9], have been widely studied and modeled. However, the effect of vulcanisation is rarely considered, because the focus of prior studies has been primarily on the cured rubber. Curing conditions affect the viscoelastic behaviour of elastomers and the final properties, and they determine the manufacturing process [10, 11]. On one hand, there are many types of thick rubber products, such as tire and conveyor belt, whose DOC is non-uniform across the section [12]. For accurate prediction of their final properties, non-uniform vulcanisation effects cannot be ignored. On the other hand, the variation of mechanical behaviour in the curing process is one of the key factors for quality control. At

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the beginning of curing, few crosslinking reactions occur, the average molecular weight increases slightly, and the viscosity decreases when curing temperature increases. When gelation occurs, the flow is arrested. The main effect of crosslinking on dynamic properties is that of increasing the elastic modulus since molecular chain motions are restricted by crosslinks. The elastic modulus increases in the curing process, while the loss modulus is little affected by the curing [13]. When the crosslink density is high, the motion of chains is significantly hindered, which can cause an increase of loss modulus and glass transition temperature (T_g). Studies on the mechanism of reinforcement by fillers are currently popular focus areas for research [14]. Similar to uncured filled compounds, time–temperature superposition principle is applicable for cured filled rubber [9, 15, 16]. However, little relevant research on exists understanding the role of vulcanisation in changing particle–particle and/or particle–polymer interactions.

Viscoelastic properties are often determined with steady-state oscillation tests. The approach is usually referred to as dynamic mechanical analysis (DMA) or dynamic mechanical thermal analysis (DMTA). However, the DMA method is not widely used to study the vulcanisation process of rubber, because the pressure which is a necessary condition in vulcanisation process cannot be applied in DMA test procedure. Therefore, the rubber process analyser (RPA) with a closed cavity is used to study the curing process. The effect of strain dependence of complex dynamic modulus of filled rubber has been known as the Payne effect. The storage modulus decreases from initial plateau value to a high strain plateau value with increasing strain amplitude at constant temperature and constant frequency. Meanwhile, the loss modulus shows a single peak with increasing strain amplitude over a certain range of amplitude (0.01–100%). The first phenomenological quantitative model to describe the Payne effect of carbon black filled rubber was presented by Kraus in 1984 [18]. The Kraus model has been deduced by assuming that the carbon black contacts break and reform according to functions of strain amplitude. Most of the parameters contain physical meaning. These parameters are very helpful to study the effect of DOC on viscoelasticity.

In this study, the viscoelastic properties of silica-filled natural rubber are studied in detail in the curing stage. Specimens are loaded with harmonic deformations at different DOCs and amplitudes. The storage and loss moduli were recorded. The changes that occur in the rubber chain network and the interactions between rubber chains and filler are discussed. The effect of curing conditions on amplitude-dependent dynamic modulus is also discussed and the Kraus model is employed.

Experimental

Materials

Table 1 shows the formula of filled natural rubber (NR). The raw NR was masticated first on a two-roll mill by passing it through the rolls about 11 times. After that, activator ZnO, co-activator stearic acid, antioxidant, and accelerator *N*-(oxidiethylene)-2-benzothiazolyl sulfonamide (NOBS) were added and mixed for 3 min with a rolling bank and five cuts on each side. Then, silica and TESPT were added at the same time and mixed for 5 min. Finally, sulfur was added and mixed for 2 min and five additional passes. The temperature during mixing was controlled below 90 °C. The temperature did not get high enough for the reaction with silane coupling agent which is normally required to get 160 °C. Therefore, little or no coupling was probably achieved between filler and polymer. The compound was stored at room temperature for at least 8 h.

Characteristics of the cure kinetics

To investigate the dynamic viscoelasticity and the Payne effect of the silica-filled rubber at different DOC, the test pieces at different DOC should be prepared. At first, the cure kinetics should be measured. The simplest experiment

Table 1 Material formula of NR filled with silica

Raw material	Mass fraction (phr)	Manufacturer
Natural rubber (NR)	100	Xishuangbanna Jingyang Rubber Co., Ltd.
Zinc oxide	5	Maofeng Chemical Co., Ltd
Stearic acid	2	Zhengzhou Alpha Chemical Co., Ltd
Antioxidant 4010	2	Kailun Chemical Co., Ltd
N-(Oxidiethylene)-2-benzothiazolyl sulfonamide (NOBS)	0.75	Nanjing Shuguang Silane Chemical Co., Ltd.
S	2.5	Shanghai Dunmei New Material Technology Co., Ltd
TESPT	0.75	Rizhao Lanxing Chemical Co., Ltd.
Silica (ZEOSIL 155)	30	Qingdao Rhodia Co., Ltd.

to characterise vulcanisation kinetics is the evolution of crosslinks, which is commonly called the cure curve, and can be measured using an ODR. RPA 8000 which is made by GOTECH according to ASTM-D6204, D5289, D6601, and ISO-6502 was employed to characterise the curve. The material sample was cured at 170 °C, the frequency and amplitude of rotation angle were both fixed at 1.7 Hz and 0.5°. The DOC was calculated from elastic torque-cure time curve (also called cure curve), which can be given by the following:

$$\mathrm{DOC} = \frac{S' - S'_{\mathrm{min}}}{S'_{\mathrm{max}} - S'_{\mathrm{min}}}, \tag{1}$$

where S' is the elastic component (in-phase with strain) varying with cure time, subscripts min and max denote maximum and minimum values of S', respectively. The cure curve is acquired by RPA 8000 to determine the cure time for different DOC before the samples were prepared. The seven levels of DOC were selected and the cure time for different DOC is listed in Table 2.

To stop the cure reaction, the fast cooling method [17] is employed. Then, the sample cured to different DOC was quickly taken out of the die and dropped into water, which was fixed at 25 °C. The sample temperature quickly fell to the lower temperature where the reaction can be neglected.

Payne effect and Kraus model

The Payne effect is a particular strain dependence of complex dynamic modulus for filled rubber. When strain amplitudes increase, a decrease in storage modulus and a maximum in loss modulus can be observed. It can be attributed to the deformation induced changes in material microstructure, which lead to breakage and reforming of weak physical bonds between the filler aggregates or between filler and rubber. The first phenomenological model to describe the Payne effect is presented by Kraus [18]. The Kraus model can be expressed by the following [19–21]:

$$G'(\gamma) = G'_{\infty} + \frac{G'_0 - G'_{\infty}}{1 + \left(\gamma/\gamma_{\mathrm{C}}\right)^{2m}} \tag{2}$$

$$G''(\gamma) = G''_{\infty} + \frac{2\left(G''_{\mathrm{m}} - G''_{\infty}\right)\left(\gamma/\gamma_{\mathrm{C}}\right)^{m}}{1 + \left(\gamma/\gamma_{\mathrm{C}}\right)^{2m}}, \tag{3}$$

where γ_{C} is the characteristic value of the strain amplitude, at which the loss modulus reaches its maximum G''_{m}. G'_0 is the storage modulus for small strain amplitudes (usually < 0.01%); G'_{∞} and G''_{∞} are the asymptotic plateau values of the storage and loss modulus at large strain amplitudes, respectively; m is a non-negative phenomenological exponent to fit the experimental data. It decreases slightly with increase in frequency, varying from 0.6 to 0.4 [19, 21–23]. This model is widely used for cured rubber and it is first time to be introduced for uncured rubber and rubber during curing in this paper.

Results

The storage moduli G' and the loss moduli G'' are calculated based on the stress responses to the strain excitations. Material parameters of Kraus model are listed in Table 3. The exponent m was fixed at 2/3 which was proposed by Klüppel and Heinrich [24]. The different values of γ_C were acquired by fitting the storage moduli G' and the loss moduli G'' of the same sample. Therefore, the γ_C^* was used to for loss moduli G''.

Storage moduli of silica-filled NR compounds under different DOC are shown in Fig. 1. The agreement with

Table 2 The cure time for seven levels of cure extent

DOC (%)	2	10	23	50	75	90	100
Cure time (s)	60	78	108	138	204	270	324

Table 3 Material parameters from least square fits of Kraus model to the experimental data for sample with different DOCs

DOC (%)	G'_{∞} (MPa)	G'_0 (MPa)	γ_{C} (%)	G''_{∞} (MPa)	G''_{m} (MPa)	γ^*_{C} (%)
2	51.6	226.3	66.1	55.8	70.7	1.1
10	64.1	316.3	74.5	54.8	72.0	1.1
23	137.8	475.5	60.6	55.9	64.2	1.1
50	124.2	505.5	62.9	52.3	65.8	0.94
75	145.3	562.4	52.3	34.9	58.5	1.9
90	122.3	611.2	56.8	44.2	61.2	2.8
100	160.7	677.5	47.1	42.6	63.4	3.4

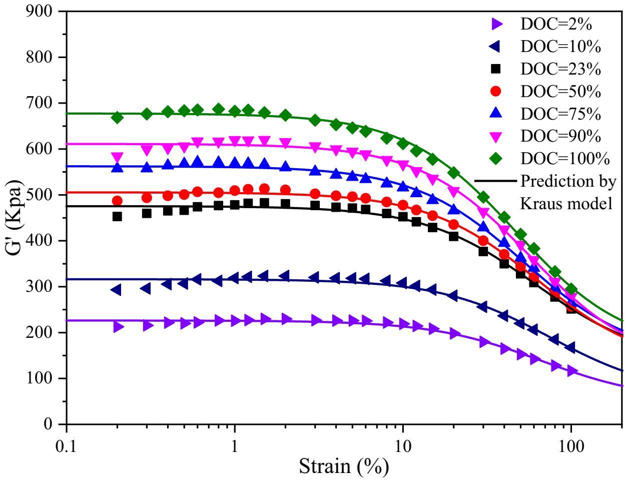

Fig. 1 The storage modulus of sample with different DOCs

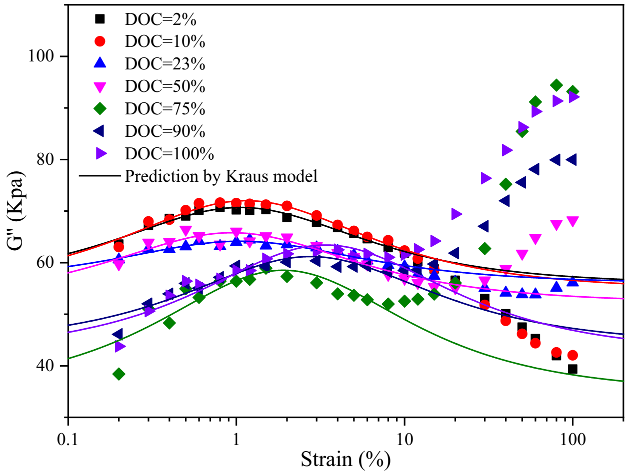

Fig. 2 The loss modulus of sample with different DOCs

the Kraus model is very good, except for very small differences at very low strains. These differences might be attributed to an experimental error at very low strain.

It can be seen that there is a region where a storage modulus is independent of shear strain, or the so-called linear viscoelastic region (LVE) in the lower shear strain. The storage modulus G' increases when DOC increases in small strains. In addition, the dependence of G' on shear strain is more pronounced when DOC increases. The result could be explained by the breakdown of the filler–filler transient networks (usually known as the Payne effect) [9]. The gelation point is the key point that distinguishes the solid and fluid. The 23% DOC data (denote filled square) are the results acquired from the sample which is cured to the gelation point and cooled down. It is shows that the character of a viscoelastic fluid is different from the character of solid. Before the gelation point, the dramatic increasing of G' is taken place, especially at the large strains, which is greater than 10%.

In general, there are multiple types of networks in the rubber which is proved by many researchers. They can be roughly classified into three types, such as rubber networks, filler–rubber networks, and filler–filler networks. Because of the similar effect on viscoelastic property, the filler–rubber networks and filler–filler networks can be considered as filler networks. The increase of G' can be considered as due to two main reasons. First, the chains of rubber react with each other in the curing process. The rubber network changes from the entanglement networks to the crosslink networks. Second, the interaction between rubber chains is enforced, so that the rigidity of rubber network increases. Due to existing of TESPT, the bond rubber at the surface of silica particle is formed as crosslinking proceeds. The interaction between filler and rubber is also enhanced.

The loss modulus (G'') is an important parameter that indicates the dissipated energy of the viscoelastic material. The relations between G'' and strain are complicated, which is shown in Fig. 2. At 2% and 10% DOC, there is a good agreement with the Kraus model. Above 10% DOC, as DOC increases, the agreement remains good at low strains, but at high strains, the observed G'' shows a large rise with increasing strain, while the model predicts a drop. G'' at 100% strain increases with increasing DOC, but 75% DOC is anomalous with the largest G'' at 100% strain.

When the strain increases, G'' increases first, then decreases, and finally increases straightly to a maximum value. This trend is more notable in the higher DOC sample. It may be caused by the interaction between filler and rubber is destroyed by deformation. When DOC is less than 10%, G'' decreases at lager deformation (strain > 40%). The main reason is that the bound rubber between rubber and silica is not formed. As the bound rubber increases, the more rapidly increasing of G'' is observed. However, when DOC is about 75%, the results show a more significant increase for G''. It may be explained by that the strength of bound rubber was weak at low extent of cure, but the strength is enhanced when the extent of cure larger than 90%.

The results of the damping factor (tanδ) are shown in Fig. 3. It is known that G' is related to the density of crosslinking, which is reduced with increasing dynamic shear strain, while G'' is related to the dissipated energy which is generally caused by the molecular slippage as well as breakdown of the filler transient network during deformation. The damping factor firstly increases with the strain increasing in small strain (< 1%) and more observably at larger strain (> 10%). For the sample with low DOC, there also exists a slightly decrease of tanδ at middle strain (1–10%). In other words, the increase in tanδ with shear strain is a result of filler network disruption and

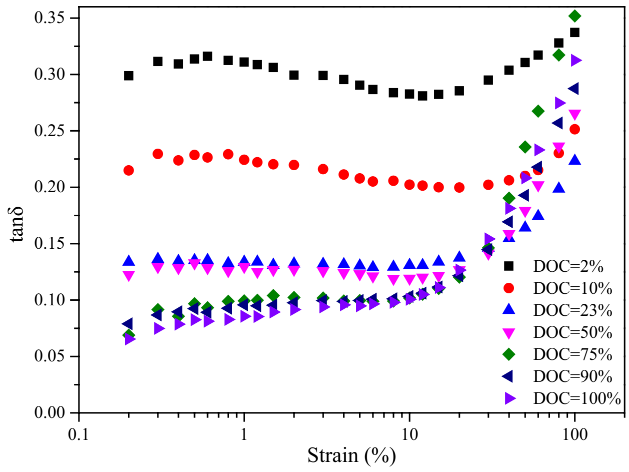

Fig. 3 The loss tangent of sample with different DOCs

molecular chain slippage. Notably, the filler networks were not destroyed with small deformation. The loss moduli decrease as DOC increases; meanwhile, the storage moduli increase significantly as DOC increases, so that the damping factor at lower strain markedly decreases with increasing of DOC.

Conclusion

Viscoelastic properties of silica-filled natural rubber compounds with different DOC were investigated by RPA8000. The following conclusions could be drawn by the following:

1. The storage modulus in the linear viscoelastic region is clearly related to the crosslinking density, which is always proportional to DOC.
2. The Kraus model is used to fit the test data, which is widely used to describe the Payne effect. The relationship between the parameters of Kraus model and curing degree is obtained at low strain ($< 10\%$). The storage modulus at low strains is not proportional to the DOC, but it does increase with increasing DOC. The storage modulus at large strains does vary with DOC. Although the increases are smaller than at low strains, the percentage increases at 100% strain appear to be similar to those observed at low strains.
3. The characteristic value of the strain amplitude is shifted to larger strain and the maximum loss modulus at strain less than 10% decreases with increasing of DOC, except for 75% DOC with a lower maximum than 90% and 100% DOC. At higher strains, the maximum loss modulus increases with increasing DOC, although again 75% DOC is anomalous. Besides, the deviation between Kraus model and experiment is obtained when the strain is larger than 10%. Here, the loss modulus increases with increasing of the strain amplitude. As discussed above, the deviation from the Kraus model, which is observed at higher strains, increases with increasing DOC. The interaction between silica filler and rubber chain may be responsible for the observed deviation.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Song CZ, Che YX, Zhang ZG, Du AH (2011) Effect of silane coupling agent on filler network structure and dynamic mechanical properties of carbon black/silica reinforced nitrile rubber, China. Synth Rubber Ind 34(2):128–132
2. Attard MM, Hunt GW (2004) Hyperelastic constitutive modeling under finite strain. Int J Solids Struct 41(18–19):5327–5350
3. Arruda EM, Boyce MC (1993) A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials. J Mech Phys Solids 41(2):389–412
4. Drozdov AD, Dorfmann A (2003) Finite viscoelasticity of filled rubber: experiments and numerical simulation. Arch Appl Mech 72(9):651–672
5. Wu JD, Kenneth ML (2000) Multiaxial and time dependent behavior of a filled rubber. Mech Time Depend Mater 4(4):293–331
6. Song Y, Zeng L, Zheng Q (2017) Reconsideration of the rheology of silica filled natural rubber compounds. J Phys Chem B 121(23):5867–5875
7. Diani J, Fayolle B, Gilormini P (2009) A review on the Mullins effect. Eur Polym J 45(3):601–612
8. Fu W, Wang L (2016) Research on Payne effect of natural rubber reinforced by graft-modified silica. J Appl Polym Sci 133(36):43891–43898
9. Gan S, Wu ZL, Xu H, Song YH, Zheng Q (2016) Viscoelastic behaviors of carbon black gel extracted from highly filled natural rubber compounds: insights into the Payne effect. Macromolecules 49(4):1454–1463
10. Studebaker ML, Beatty JR (1972) The oxidative hardening of SBR. Rubber Chem Technol 45(2):450–466
11. Suetsugu Y, White JL (1983) The influence of particle size and surface coating of calcium carbonate on the rheological properties of its suspensions in molten polystyrene. J Appl Polym Sci 28(4):1481–1501
12. Wang YS, Su BL, Wu J (2012) Simulation and optimization of giant radial tire vulcanization process. Procedia Eng 31(18–19):723–726
13. Schaefer RJ (1995) Tech service: dynamic properties of rubber. Rubber World 211(4):16–19
14. Neogi C, Bhattacharya AK, Bhowmick AK (1989) Dynamic mechanical analysis of carbon black filled rubber compounds under swollen conditions. Rubber Chem Technol 62:651–659

15. Ruddock N, James PW, Jones TER (1993) Modelling the linear viscoelasticity of unfilled and carbon black loaded elastomers. Rheol Acta 32(3):286–292
16. Funt JM (1988) Dynamic testing and reinforcement of rubber. Rubber Chem Technol 61(5):842–865
17. Chambon F, Winter HH (1985) Stopping of crosslinking reaction in a PDMS polymer at the gel point. Polym Bull 13(6):499–503
18. Kraus GJ (1984) Mechanical losses in carbon-black-filled rubbers. Appl Polym Symp 39(1):75–92
19. Hu XL, Luo WB, Liu X, Huang YJ, Bu JL (2013) Temperature and frequency dependent rheological behavior of carbon black filled natural rubber. Plast Rubber Compos 42(10):416–420
20. Kim BK, Youn SK (2001) A viscoelastic constitutive model of rubber under small oscillatory load superimposed on large static deformation. Arch Appl Mech 71(11):748–763
21. Cho JH, Youn SK (2006) A viscoelastic constitutive model of rubber under small oscillatory load superimposed on large static deformation considering the Payne effect. Arch Appl Mech 75(4–5):275–288
22. Lion A, Kardelky C (2004) The Payne effect in finite viscoelasticity-constitutive modelling based on fractional derivatives and intrinsic time scales. Int J Plast 20(7):1313–1345
23. Huber G, Vilgis TA, Heinrich G (1996) Universal properties in the dynamical deformation of filled rubbers. J Phys Condens Matter 8(29):409–412
24. Heinrich G, Klüppel M (2002) Recent advances in the theory of filler networking in elastomers. In: Lee K-S (ed) Advances in polymer science, vol 160. Filled elastomers drug delivery systems series. Springer, Berlin, pp 1–44

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