

## *Supporting information for*

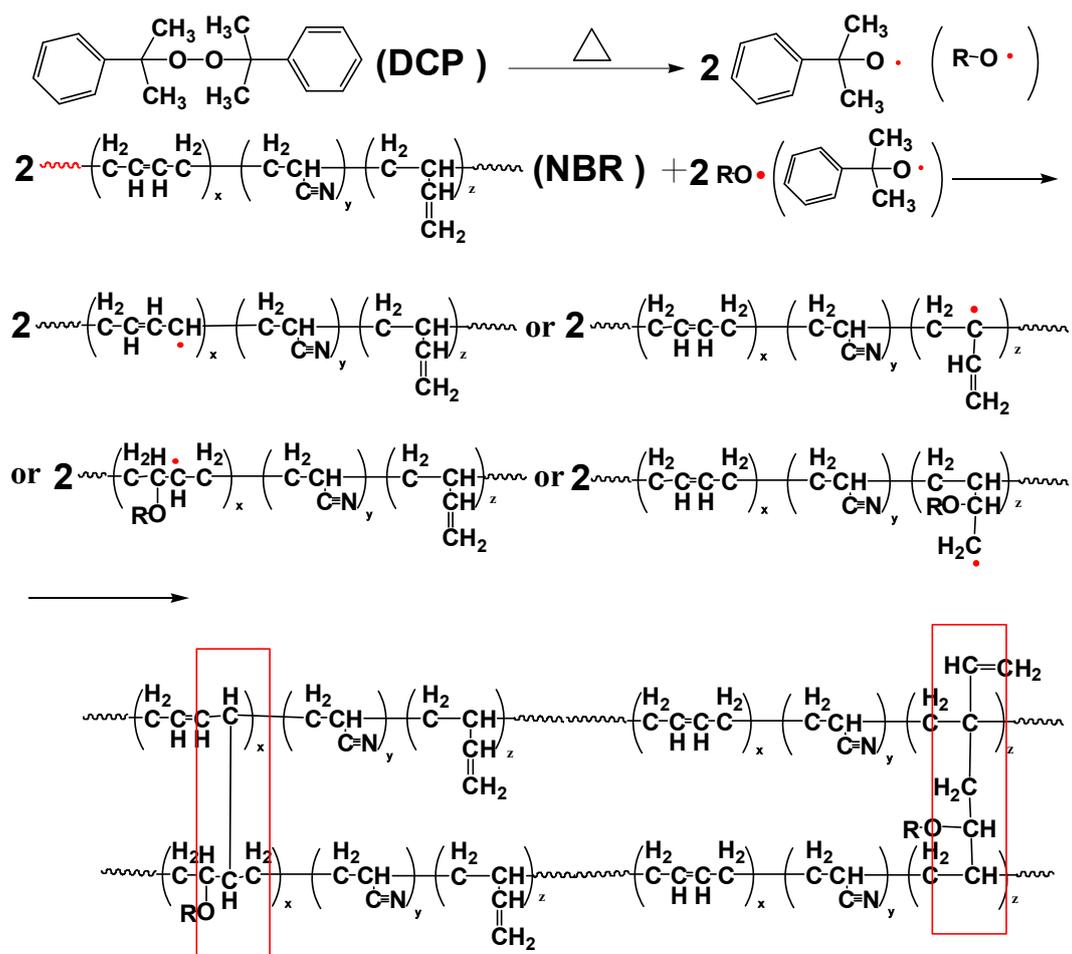
### **Rheology of nitrile rubber with hybrid crosslinked network comprised of covalent bonding and hydrogen bonding**

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#### **Crosslinking Mechanism of NBR with DCP and MBA :**

Vulcanization mechanism of nitrile rubber (NBR) by dicumyl peroxide(DCP) has been clarified,<sup>[1-3]</sup> as shown in Scheme 1. As a vinyl monomer with amide group, chemical property of N,N-methylenebis acrylamide (MBA) is similar to acrylamide and its free radical reaction can be initiated by a variety of systems such as azo initiator, organic peroxide initiator, inorganic peroxide initiator, redox initiator system, radiation, etc.<sup>[4-8]</sup> Furthermore, MBA also acts as a crosslinking agent due to the presence of two carbon carbon double bonds in a single molecule. Although azodiisobutyronitrile (AIBN) and benzoyl peroxide (BPO) is often used as MBA initiators besides inorganic initiators, DCP is chosen as the initiator of NBR vulcanization by MBA in in this work due to the vulcanization temperature and efficiency of NBR. It is reasonably believed that the initiation mechanism of MBA by DCP is similar to that of BPO<sup>[6-8]</sup>, thus the vulcanization mechanism of NBR by MBA is proposed as indicated by Scheme 2: DCP is divided into two alkoxy radicals at high temperature, then they randomly attack of alkoxy radicals on active sites of NBR and MBA molecules (allylic hydrogen or carbon carbon double bonds) to form rubber macromolecule free radical and MBA free radical. NBR rubber network with three dimensional cross-linked network structure appears by coupling of various free radicals.

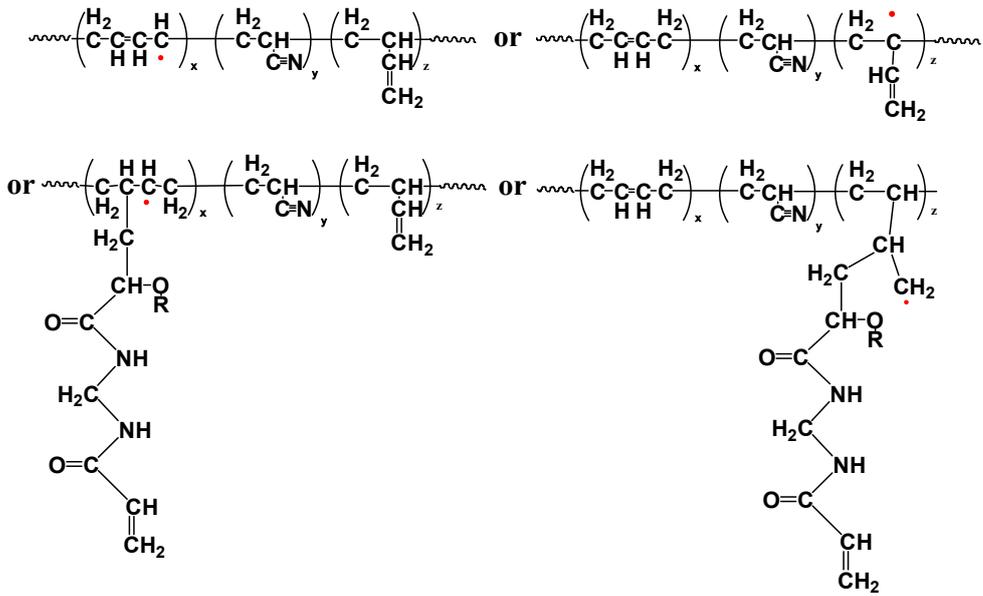


Scheme 1 Vulcanization mechanism of NBR by DCP

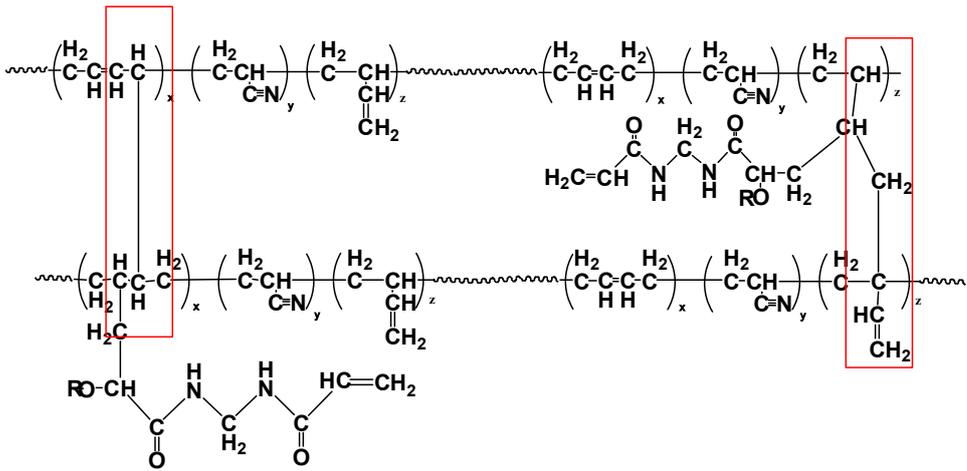


or

four kinds of free radical



→



Scheme 2 Vulcanization mechanism of NBR by complex vulcanizing agent of DCP and MBA

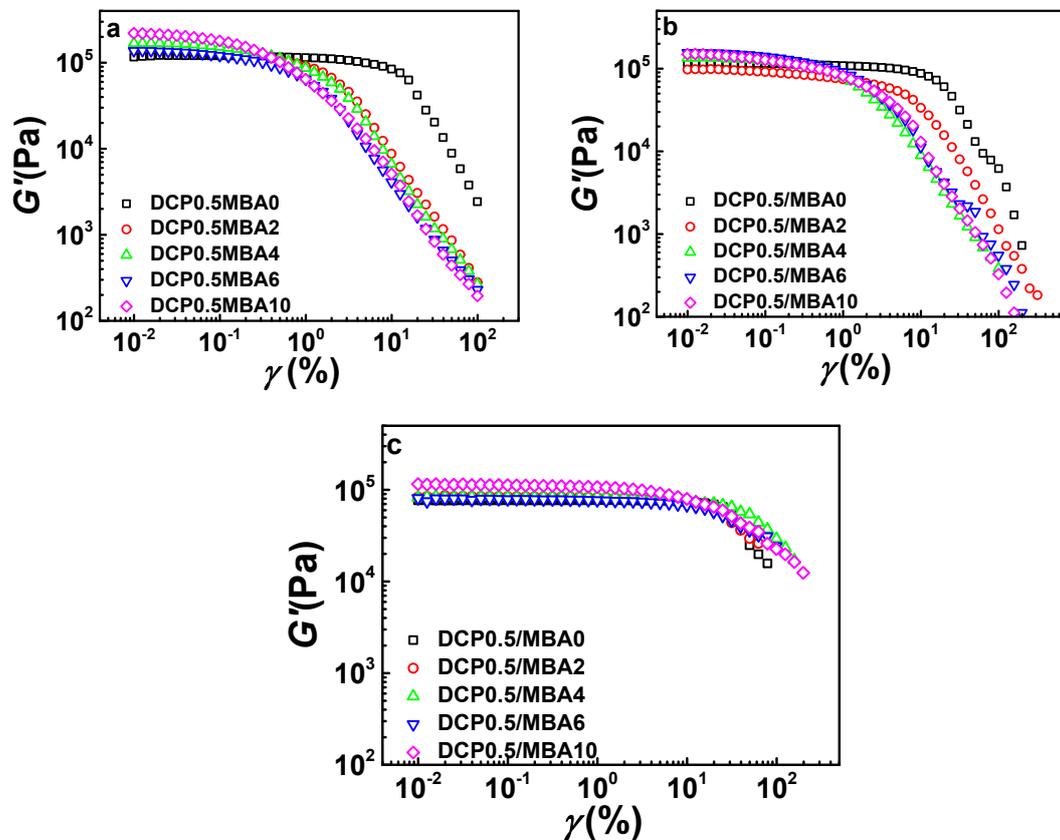


Figure S1 Strain sweep of vulcanized NBR samples with different MBA amount at (a)40°C, (b)60°C, (c) 100°C respectively.

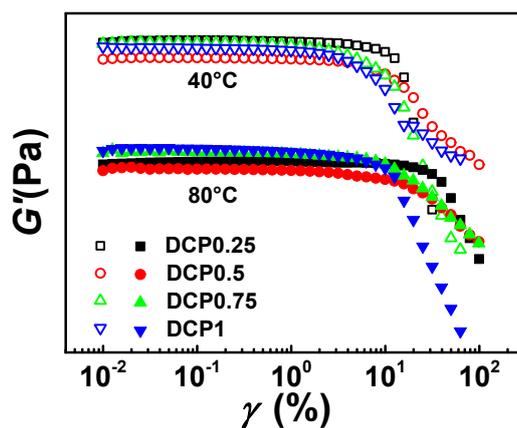


Figure S2 Strain sweep of samples vulcanized with different DCP amount at 40°C(open), 80°C(solid), respectively.

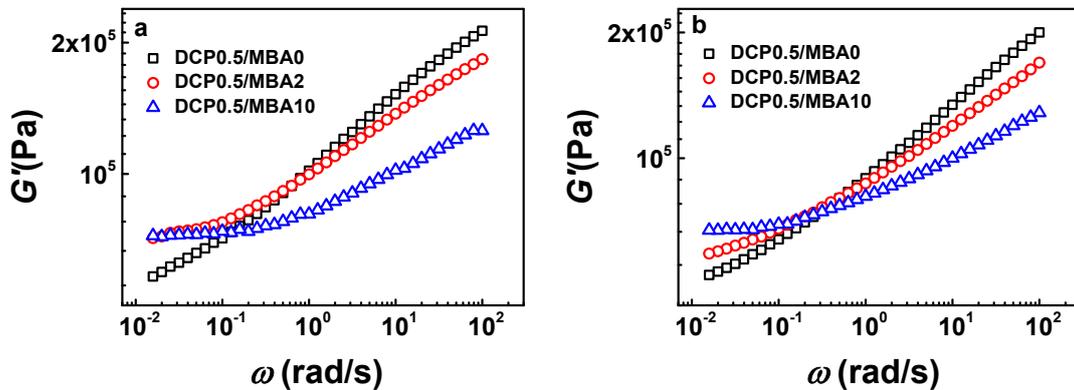


Figure S3 (a)  $G'$  of vulcanized NBR samples with different MBA amount versus angular frequency at 45°C. (b)  $G'$  of vulcanized NBR samples with different MBA amount versus angular frequency at 60°C.

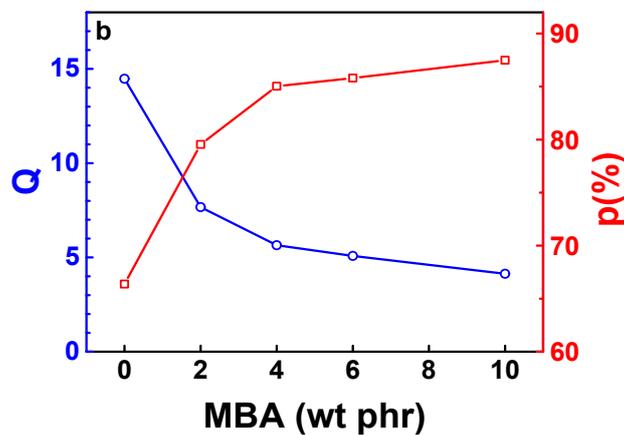


Figure S4 Influence of MBA amount on crosslinking degree of vulcanized samples with 0.5phr DCP.

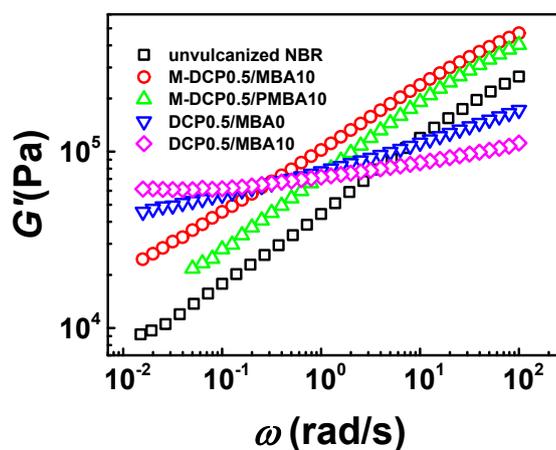


Figure S5  $G'$  of unvulcanized NBR, M-DCP0.5/MBA10(mixture of 0.5phr DCP and 10phr MBA), M-DCP0.5/PMBA10(mixture of 0.5phr DCP and 10phr Poly(MBA)), DCP0.5/MBA0, DCP0.5/MBA10 versus angular frequency at 80°C.

Compared with unvulcanized NBR and DCP0.5/MBA10, M-DCP0.5/MBA10 and M-DCP0.5/PMBA10 behave a higher  $G'$  in high frequency region. This phenomenon indicates that non-reacted MBA and DCP enhance  $G'$  and discrepancies in the high frequency does not result from plasticizing effects due to non-reacted MBA and DCP.

## References

1. L. D. Loan, *J. Appl. Polym. Sci.*, 2005, 7, 2259-2268
2. J. L. Valentín, A. Rodríguez, A. Marcos-Fernández, L. González, *J. Appl. Polym. Sci.*, 2005, 96, 1-5
3. L. González, A. Rodríguez, C. Chamorro, *Rubber chem. Tech.* 1997, 69, 203-214
4. R. Suedee, V. Seechamnaturakit, B. Canyuk, C. Ovatlarnporn, G. P. Martin, *J. Chromatogr. A*, 2006, 1114, 239-249
5. G. Y. Liu, X. L. Yang, Y. M. Wang, *Polymer*, 2007, 48, 4385-4392
6. L. H. Yang, B. Bai, C.X. Ding, H. L. Wang, Y. R. Suo, *RSC Adv.*, 2016, 6, 9507-9517
7. S. Swarnalatha, R. Gopi, A. G. Kumar, P. K. Selvi, G. Sekaran, *J Mater Sci: Mater Med* 2008, 19, 3005-3014
8. Z. Xu, C. Yan, Z. Q. Liu, *Org. Lett.* 2014, 16, 5670-5673