

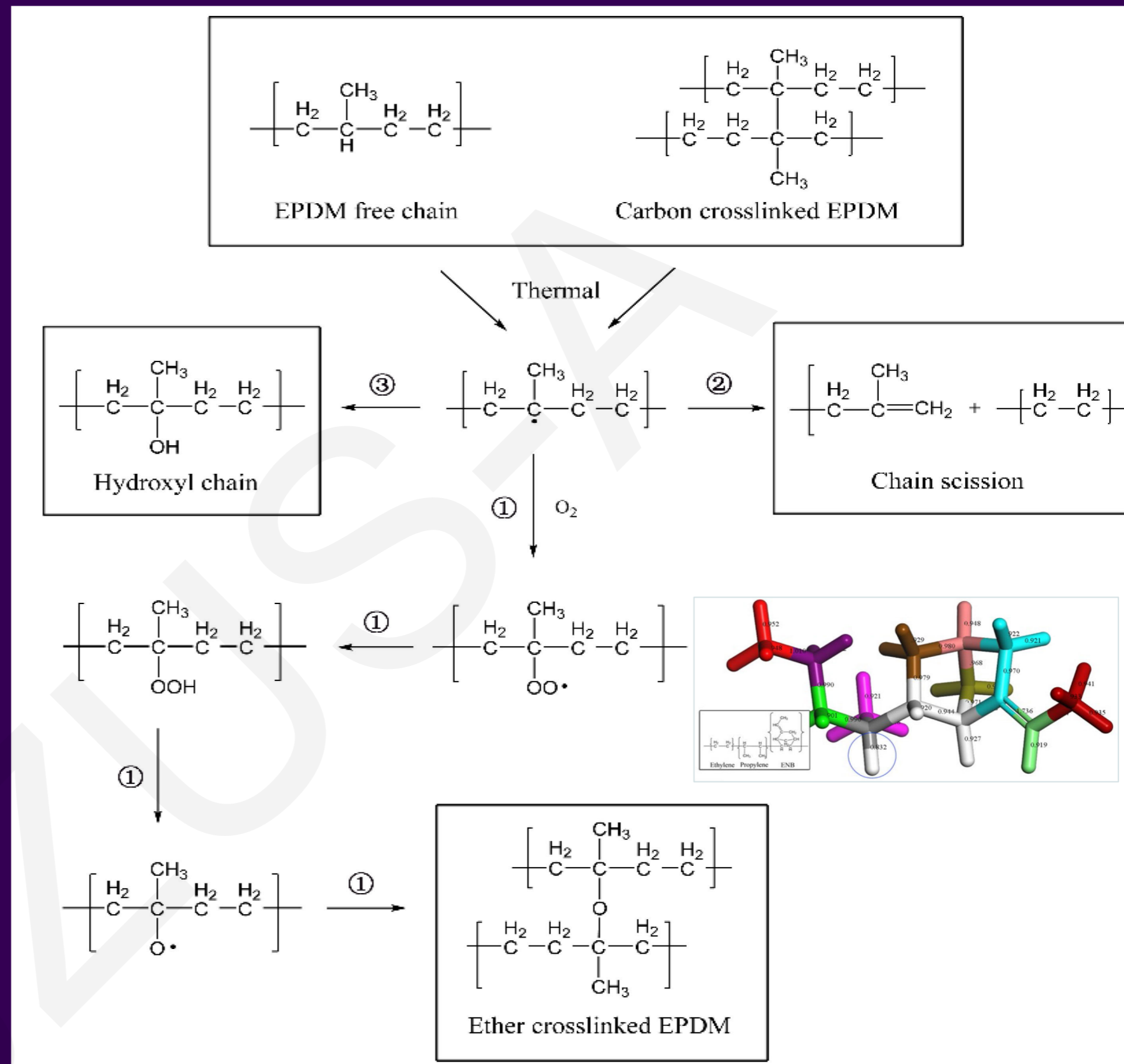
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Effect of thermo-oxidation on the dynamical and physical properties of ethylene-propylene-diene monomer elastomer

Key words:

EPDM elastomer; thermo-oxidation; glass transition temperature; free volume; cross-linking

Main chain reaction path of thermal oxidation

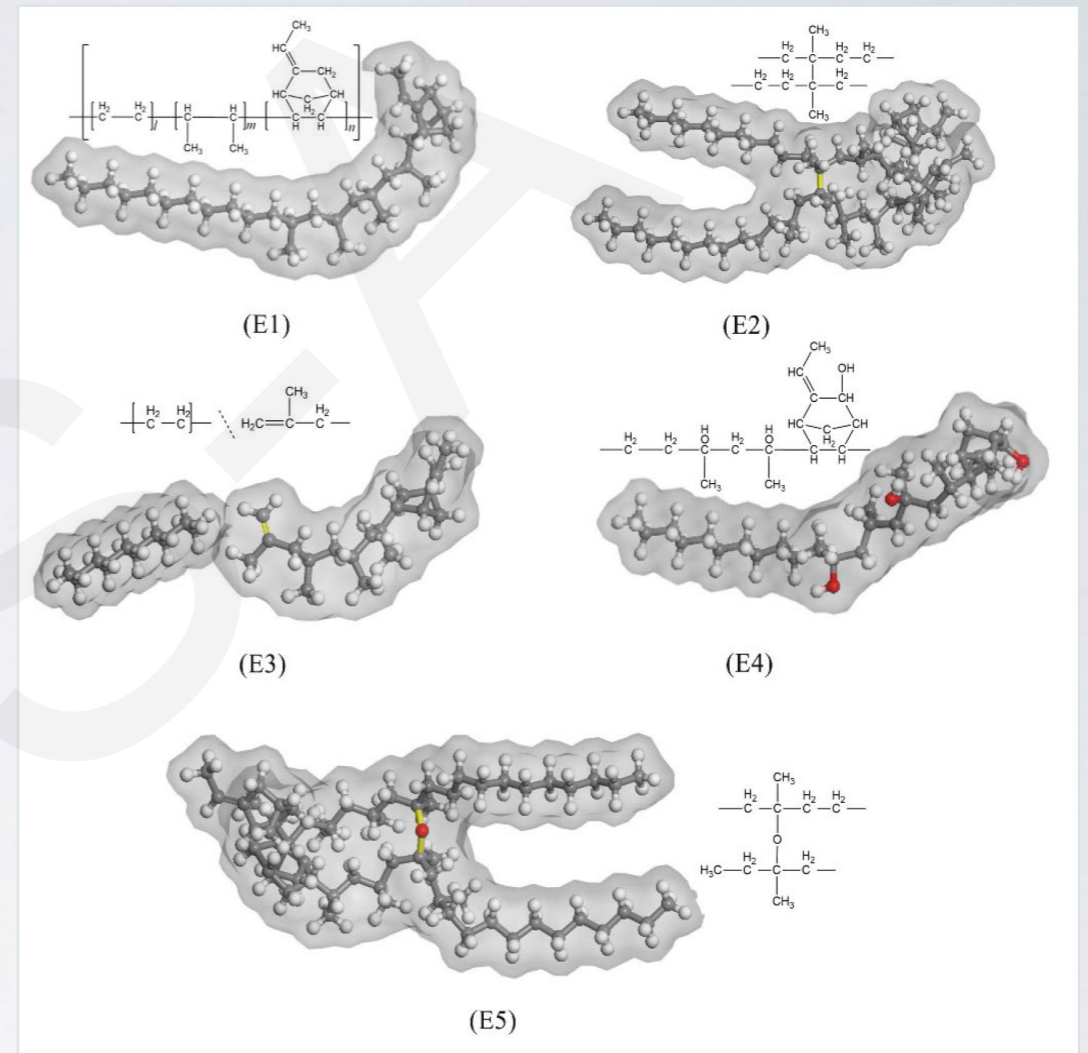


Possible thermo-oxidative reaction path of EPDM main chain, Path 1 is a cross-linking reaction in which alkoxy groups and carbon groups are combined, path 2 is a disproportionation reaction leading to chain scission, and path 3 is a combination of a carbon group and a hydroxyl group to form an alcohol

Building MD models

The ethylene, propylene, and the ENB third monomer are copolymerized in a ratio of 5:4:1, and then five types of EPDM molecules are constructed in the degradation process.

As shown in Figure, these five EPDM molecules are hydrocarbon free chain (HFC), carbon cross-linking(CCL), chain scission(CS), hydroxyl chain(HC), and ether

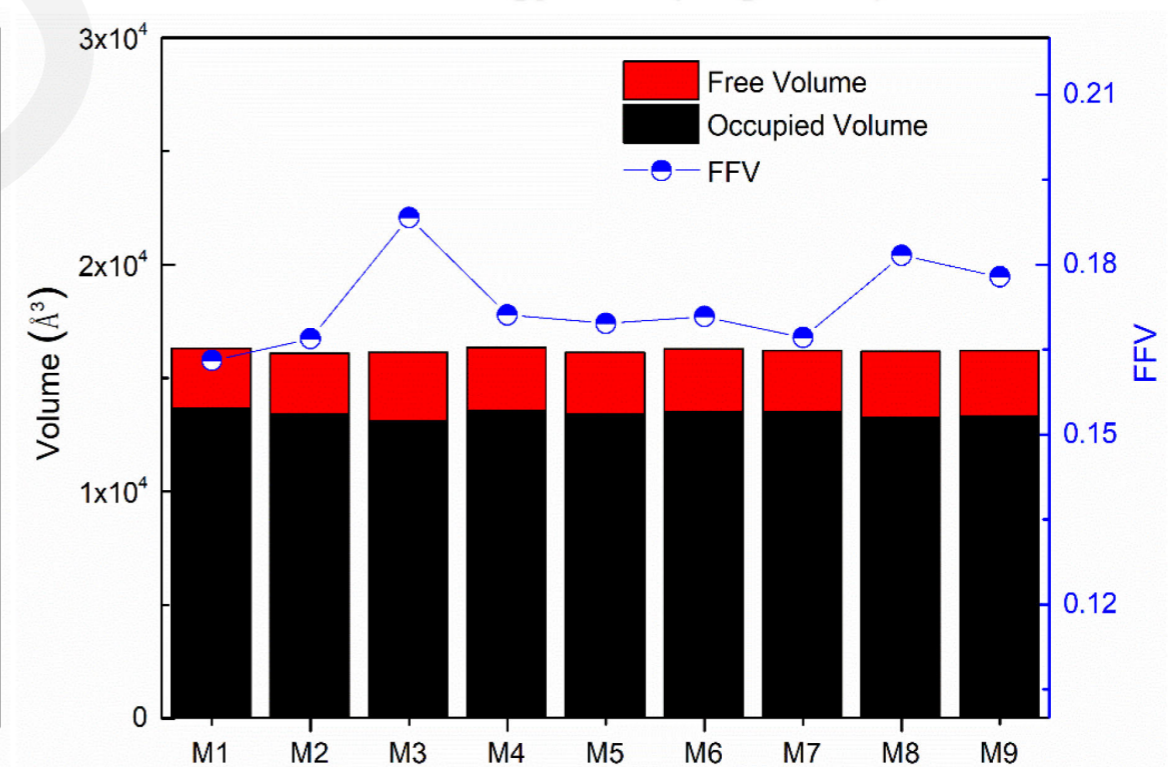
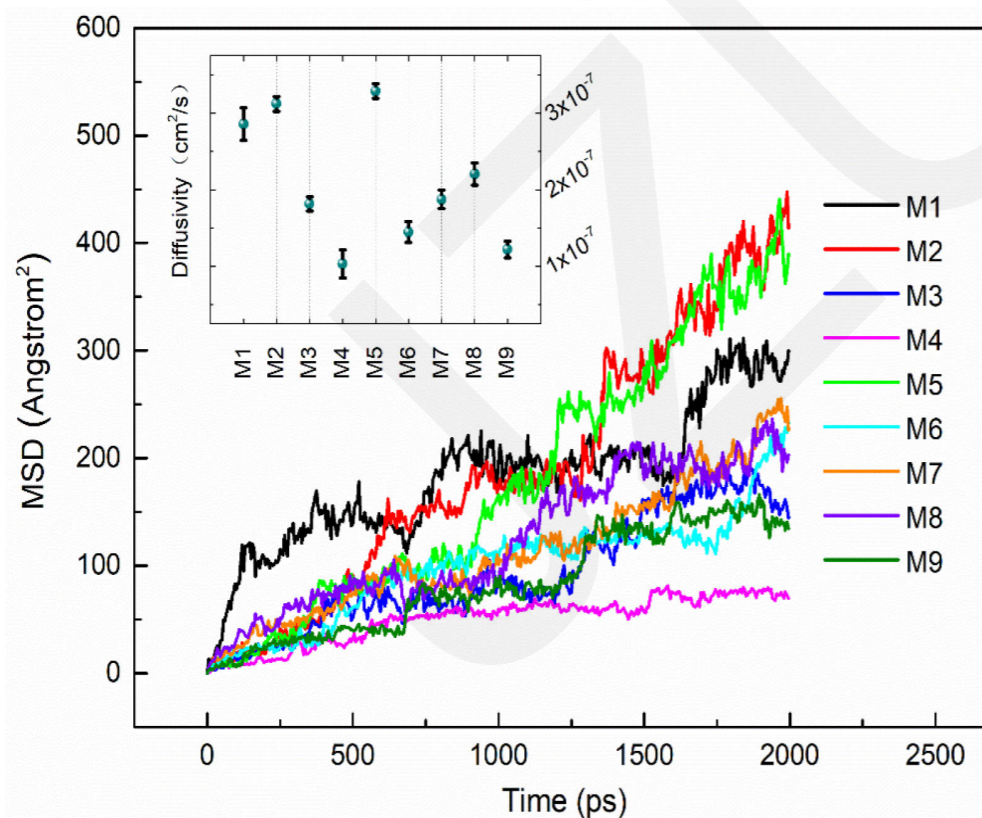
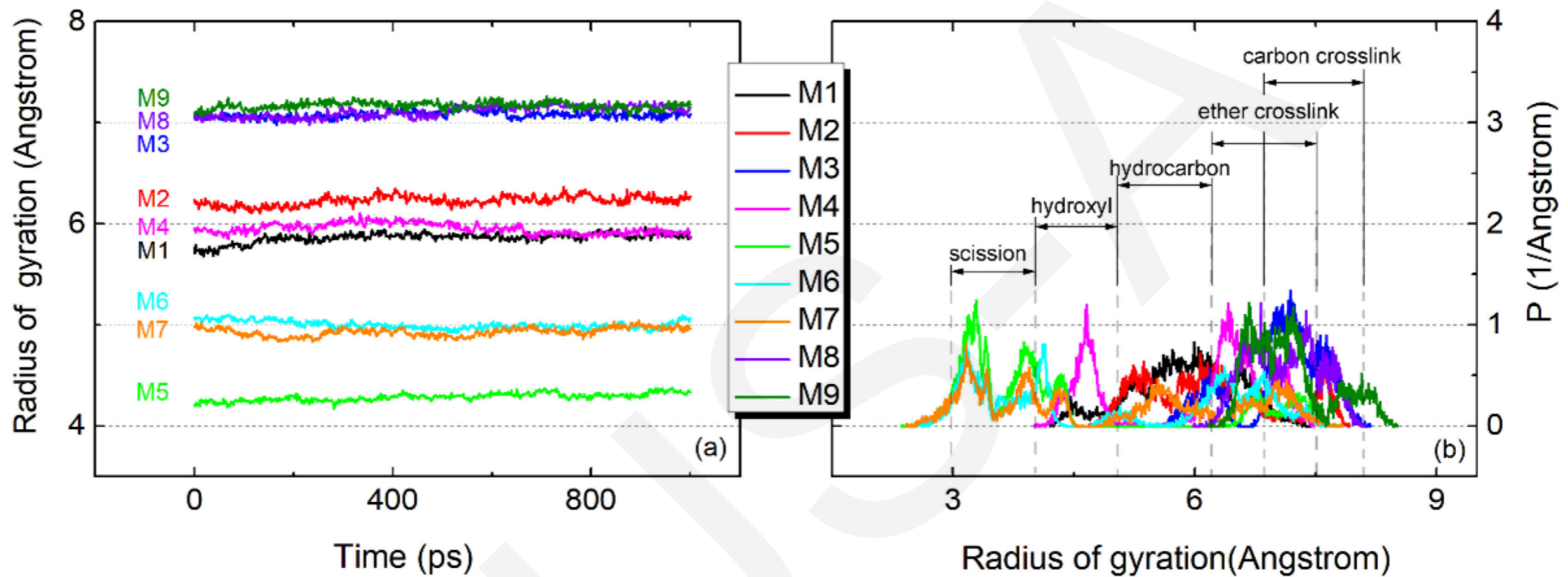


cross-linking(ECL) and are denoted by E1, E2, E3, E4, E5, respectively.

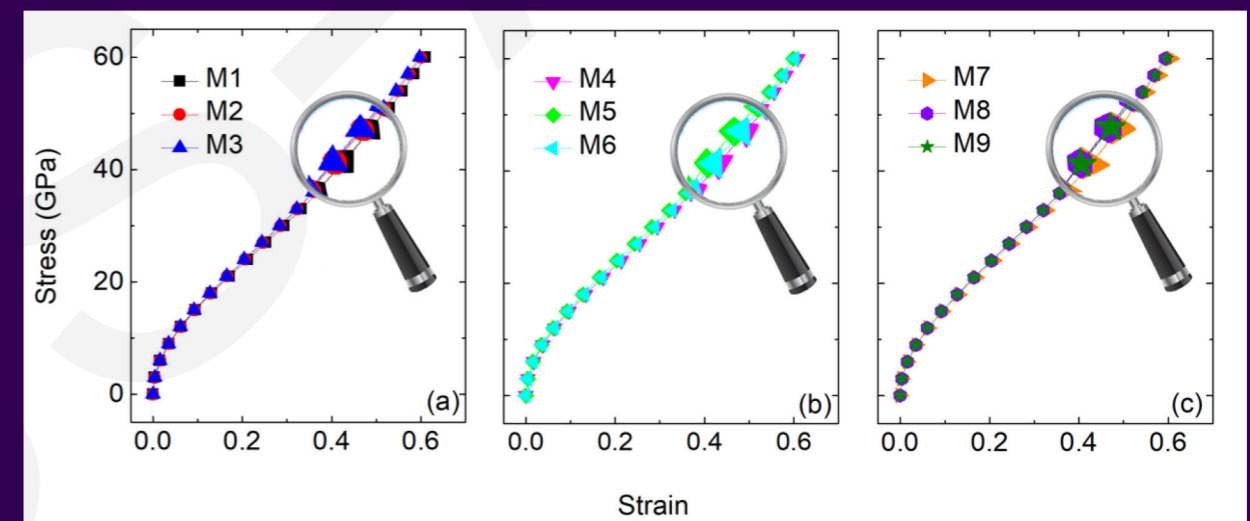
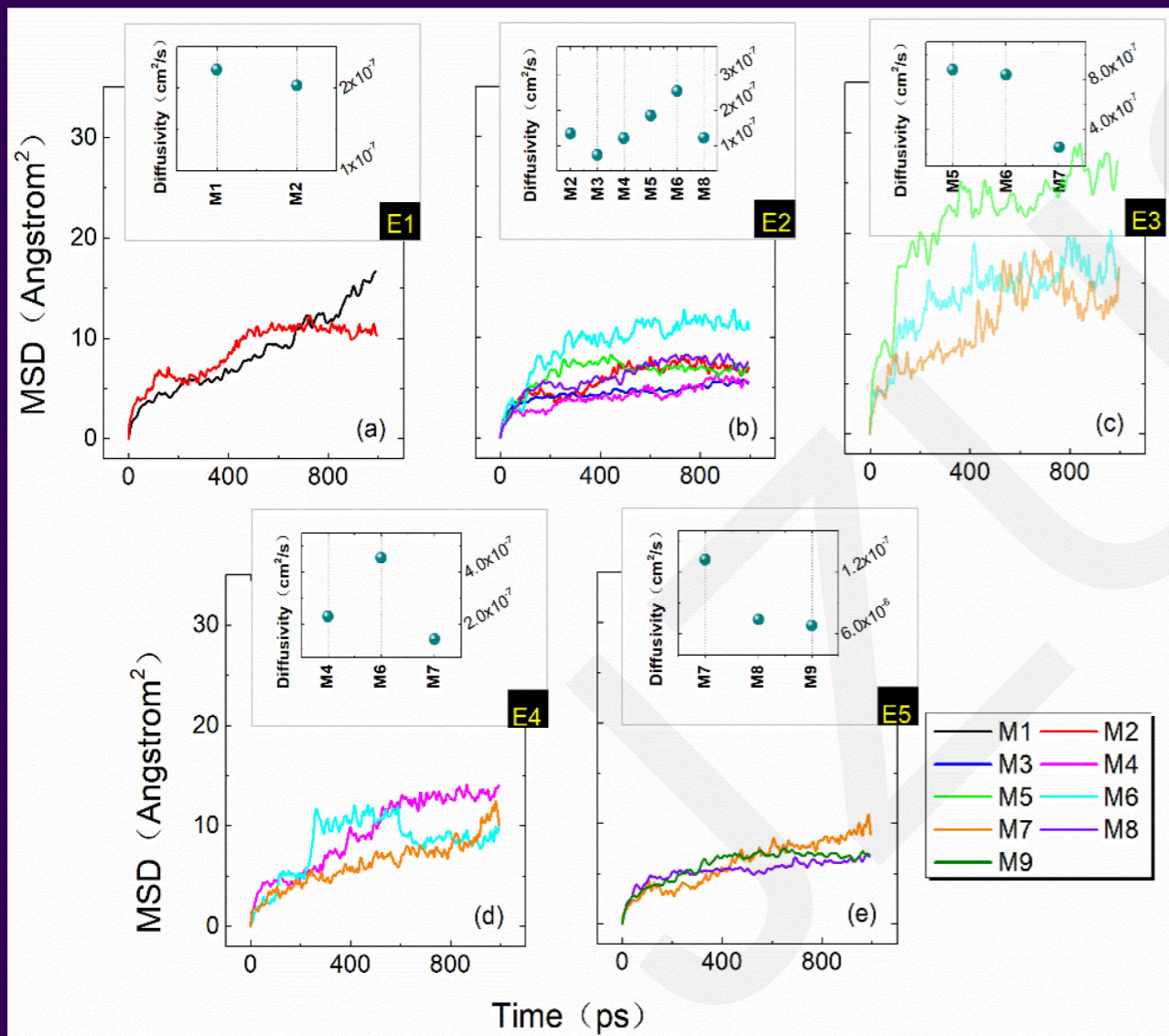
Table.1 Composition and numbering of thermo-oxidative MD models of EPDM

Number of chains	Molecular types	Netmass	M1	M2	M3	M4	M5	M6	M7	M8	M9
E1	hydrocarbon free chain	430.805	40	20							
E2	carbon crosslink	859.594		10	20	10	10	10		10	
E3	chain scission	416.778					20	10	10		
E4	hydroxyl chain	462.803				20		10	10		
E5	ether crosslink	875.593							10	10	20

Properties characterizing the space of motion of molecular chains



Properties characterizing viscoelasticity



The stress-strain behavior shows the elastic restoring force of EPDM samples under a certain compression strain, which reflects the sealing performance. The variation of EPDM stress-strain behavior with aging degree could indicate that the evolution of its elastic properties when only affected by thermal oxidation

The self-diffusion of molecular chains monitors the relaxation of EPDM

Conclusions

- ◆ The radius of gyration contributes decisively to the free volume. The carbon crosslinks (C- C) of EPDM cause the largest radius of gyration, followed by ether crosslinks (C- O- C), hydrocarbon free chains, hydroxyl chains, and chain scissions.
- ◆ Although cross-linking creates more free volume to provide space for diffusion, it restricts molecular mobility, so it is negative for diffusion, while free chain increases chain mobility and promotes self- diffusion and oxygen diffusion
- ◆ The glass transition temperature reflects the movement ability of the molecular segment and is increased by cross-linking and reduced by free chain and scission
- ◆ The uniaxial compression performance of EPDM mainly depends on the degree of crosslinking, with a higher density of crosslinking resulting in a stronger modulus. In addition, the hydroxyl group weakens the topological constraint caused by entanglement due to its polarity, leading to a decrease in modulus.