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A computational study of adhesion between rubber and metal sulfides at rubber–brass interface

Chian Ye Ling [a], Janne T. Hirvi [a], Mika Suvanto [a], Andrey S. Bazhenov [a], Tommi Ajoviita [b], Katriina Markkula [b], Tapani A. Pakkanen [a,*]

[a] Department of Chemistry, University of Eastern Finland, P.O. Box 111, FI80101 Joensuu, Finland
[b] R & D, Car Tyres, Nokian Tyres plc., P.O. Box 20, FI37101 Nokia, Finland

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ABSTRACT

Computational study at level of density functional theory has been carried out in order to investigate the adhesion between rubber and brass plated steel cord, which has high importance in tire manufacturing. Adsorption of natural rubber based adsorbate models has been studied on zinc sulfide, ZnS(1 1 0), and copper sulfide, Cu_2S(1 1 1) and CuS(0 0 1), surfaces as the corresponding phases are formed in adhesive interlayer during rubber vulcanization. Saturated hydrocarbons exhibited weak interactions, whereas unsaturated hydrocarbons and sulfur-containing adsorbates interacted with the metal atoms of sulfide surfaces more strongly. Sulfur-containing adsorbates interacted with ZnS(1 1 0) surface stronger than unsaturated hydrocarbons, whereas both Cu_2S(1 1 1) and CuS(0 0 1) surfaces showed opposite adsorption preference as unsaturated hydrocarbons adsorbed stronger than sulfur-containing adsorbates. The different interaction strength order can play role in rubber–brass adhesion with different relative sulfide concentrations. Moreover, Cu_2S(1 1 1) surface exhibits higher adsorption energies than CuS(0 0 1) surface, possibly indicating dominant role of Cu_2S in the adhesion between rubber and brass.

1. Introduction

Rubber–metal adhesion technologies play an important role in tire manufacturing. Steel cord reinforced rubber automotive tires are a standard type of tires, in which steel cords are embedded to give rubber tires a structural strength, while maintaining flexibility of rubber. Strong adhesion between rubber and steel cords is a primary requirement in order to exhibit a good performance for safe controlling automobiles as well as a pro-longed lifetime of the tire. Rubber adhesion to steel cord itself is weak, therefore, brass plated steel cords have been employed to realize strong rubber–steel cord adhesion.

Since early 1970s, the formation of copper sulfides at the rubber–brass interface has been recognized and these species are speculated to be responsible for the interfacial adhesion [1]. Both CuS and non-stoichiometric Cu_xS ($1.8 < x < 2.0$) [2,3] are formed during the curing process via interface reaction between copper in brass and sulfur in rubber compound. Also stoichiometric zinc sulfide (ZnS) co-exists as brass is an alloy of copper and zinc. The formation of copper and zinc sulfides interface was first identified by using X-ray photoelectron spectroscopy (XPS) [1,4,5], and later verified by Auger electron spectroscopy (AES) measurements [5–7]. Schematic illustration of the interfacial structure is given in Fig. 1.

Interfacial adhesion depends on many factors, including the compositional change, surface structure, and thickness of the adhesive interlayer. The adhesion is hence influenced by the composition of the rubber compound, and the inclusion of adhesion promoters such as cobalt-compounds [8]. Various studies have been carried out to achieve an understanding of the rubber–brass interface morphology and adhesion mechanism, however, it is still unclear how the chemical composition at the rubber–brass interface is altered and what is the adhesion mechanism of rubber on the brass plated steel cord surfaces. Nevertheless, two possible adhesion mechanisms have been proposed, the mechanical interlocking [9] and chemical bonding model [10].

The detailed understanding of the rubber–brass adhesion process is crucial in order to control and improve on the adhesion between rubber and brass plated steel. Thus, in the present work, we study the adsorption energetics and bonding mechanism of rubber models on both zinc and copper sulfide surfaces co-existing at adhesive interlayer. The aim is to understand the role of sulfur and other functionalities of rubber, and on the other hand, difference between zinc and copper in interfacial interaction.

* Corresponding author. Tel.: +358 405028982.
E-mail address: tapani.pakkanen@uef.fi (T.A. Pakkanen).

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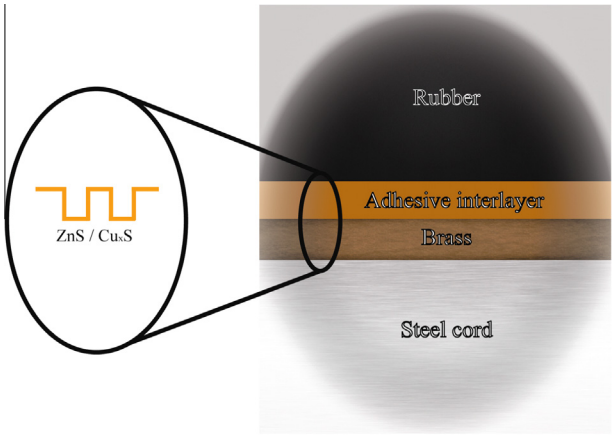

Fig. 1. Schematic illustration of interface between rubber and brass coated steel.

2. Models and methods

Adhesive interlayer between rubber and brass contains stoichiometric zinc sulfide and different stoichiometries of copper sulfide. Hence, only one bulk model was constructed for zinc sulfide, whereas two bulk models with CuS and Cu_2S stoichiometries were constructed for copper sulfide. The stoichiometry of Cu_2S was chosen due to high complexity of various non-stoichiometric Cu_xS structures, like digenite ($Cu_{1.8}S$) [11]. The most stable cubic zinc blende polymorph was used for ZnS [12], while copper sulfide models included hexagonal CuS structure and ideal high temperature phase of cubic antifluorite Cu_2S [13]. The use of idealized stoichiometric copper sulfide structures is a simplification, which does not cover all specific details of this highly complicated interfacial system. The chosen structures of ZnS, Cu_2S, and CuS are visualized in Fig. 2 and the optimized cell dimensions are compared to the experimental counterparts in Table 1. The optimization of bulk structures was performed within the experimental space group symmetries.

The lowest energy ZnS(1 1 0) [17,18], Cu_2S(1 1 1) [19], and CuS(0 0 1) [20] surfaces are cleaved from the optimized bulk structures. A (2×2) supercell is created for all the surfaces, where ZnS(1 1 0) and CuS(0 0 1) slabs consist of four atomic-layers, and

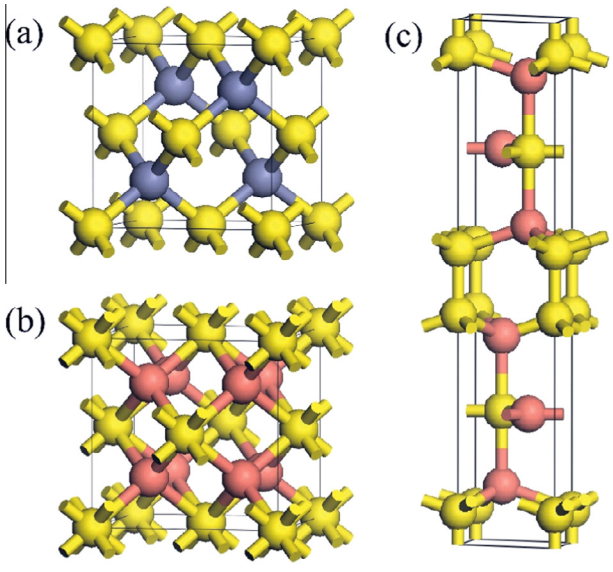

Fig. 2. Bulk structures of (a) cubic ZnS, (b) cubic Cu_2S, and (c) hexagonal CuS.

Table 1
Optimized cell dimensions (in Å) for ZnS, Cu_2S, and CuS bulk structures within the experimental space group symmetries. The experimental counterparts are given in parenthesis.

ZnS (F-43m) [14]	Cu_2S (Fm-3m) [15]	CuS ($P6_3$/mmc) [16]
a = 5.474 (5.400)	a = 5.652 (5.629)	a = 3.873 (3.788)
b = 5.474 (5.400)	b = 5.652 (5.629)	b = 3.873 (3.788)
c = 5.474 (5.400)	c = 5.652 (5.629)	c = 16.673 (16.333)

Cu_2S(1 1 1) slab consists of six atomic-layers. The lower half of atomic-layers is fixed to the bulk environment during the optimization. The corresponding surface models are visualized in Fig. 3. In adsorption calculations, adsorbate models based natural rubber structure visualized in Fig. 4, are positioned on top of the unconstrained side of the slabs. Adsorbate models include pure functional group models; methane, ethane, propane, ethene, and hydrogen sulfide, and larger models, where one of the hydrogen atoms in ethene is replaced by methyl or thiol group.

The calculations were performed at the level of DFT using the Crystal09 [21] program. The hybrid exchange–correlation functional by Perdew, Burke, and Ernzerhof (PBE0) [22–24] was employed together with the standard def-TZVP [25] basis sets for sulfur, carbon, and hydrogen atoms, and with optimized def-TZVP basis sets for zinc and copper atoms given in supplementary data (Appendix A). K-point densities of spin-paired calculations were at least 4.5 $Å^{-1}$ for zinc sulfide and 11.0 $Å^{-1}$ for copper sulfides in each periodic direction. The basis set superposition error in the adsorption energies was corrected by using counterpoise method [26].

3. Results and discussion

3.1. Adsorption on ZnS(110) surface

ZnS(1 1 0) surface plane exposes three-coordinated zinc and sulfur atoms. Adsorbate interactions with sulfur atoms are more or less repulsive, while interactions with zinc atoms are primarily attractive and hence responsible of adhesion. Adsorption energies of natural rubber based adsorbate models on top of zinc atom of ZnS(1 1 0) surface are tabulated in Table 2. There is a clear trend in the adsorption energies for pure functional group models; methane, ethane and propane exhibit only weak adsorption energies (less than -5 kJ mol^{-1}), followed by ethene (-29.8 kJ mol^{-1}), and the most strongly adsorbed hydrogen sulfide (-61.4 kJ mol^{-1}).

The optimized structures of pure functional group models on top of Zn atom of ZnS(1 1 0) surface are presented in Fig. 5(a)–(e). All saturated hydrocarbons are weakly physisorbed on the surface, whereas ethene and hydrogen sulfide interact more closely with the surface Zn atoms. This is connected to outward relaxation of the interacting Zn atom and distortion of ethene and hydrogen sulfide adsorbates from the gas phase geometries. Ethene adsorbs on the surface in the π-adsorption mode and elongation of the C=C bond and bending of its CH_2 end groups can be seen (see Table 3). The bonding can be described as π-donation from adsorbate into empty metal-states coupled with back-donation from the metal into the empty π^*-orbital of hydrocarbon. This is the so-called Dewar–Chatt–Duncanson chemisorption model [27]. Similarly, for the adsorption of hydrogen sulfide; donation of the charge from the lone pair electrons of sulfur in hydrogen sulfide to the Zn atom of the surface takes place together with back-donation of the surface electrons to hydrogen sulfide [28]. Moreover, both hydrogen atoms exhibit weak stabilizing interactions with surface sulfur atoms.

Adsorption energies of substituted ethenes on top of zinc atom of ZnS(1 1 0) surface are also tabulated in Table 2 and the optimized structures are presented in Fig. 5(f) and (g). Both substituted