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Polymer Testing

Property modelling

Rheological characterization and modelling of the rubber to metal vulcanization-bonding process

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ABSTRACT

Rubber-to-metal bonded assemblies are found in a growing number of industrial applications, particularly for the reduction of vibration, for example in the automotive industry. The so-called "vulcanization bonding process" consists of molding the rubber onto a metallic surface, previously coated with a reactive adhesive system. The vulcanization of the rubber and the curing of the adhesive then take place simultaneously during the molding cure cycle. These reactions are coupled with multiple diffusion phenomena at the interfaces between the different layers. The aim of the present work is to propose an experimental approach for the understanding and modelling of these mechanisms. The metal/adhesive/rubber reactive interface is reproduced in a rotational rheometer allowing a rheokinetic characterization of the different reactions and diffusion-reaction phenomena occurring during the process.

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1. Introduction

Despite rubber-to-metal bonded assemblies being used in a wide and growing range of industrial applications, particularly for the reduction of noise and vibration, the so-called "vulcanization bonding process" remains poorly understood [1]: It consists of molding and vulcanizing raw rubber onto a metallic surface coated with an adhesive reactive bonding layer. The rubber-to-metal assembly is thus obtained in a unique step. Contrary to "post-vulcanization bonding" techniques, it also allows the molding of complex shapes with bonded metallic inserts. Nevertheless, the process is quite complex since it involves various diffusion phenomena, along with chemisorption, bulk and interfacial crosslinking reactions [2]. Fig. 1 shows the

generally accepted schematic view of the interface in the case of a bonding layer consisting of two layers [1]: A primer, coated on the metallic substrate, and an adhesive layer in contact with the raw rubber. The total thickness of these layers is typically lower than 30 μm.

In such a complex system, various conditions have to be fulfilled in order to obtain high performance rubber-to-metal adhesion:

The first condition concerns the internal crosslinking reactions of the rubber, the primer and the adhesive, the respective kinetics of which have to be compatible within the imposed molding cure temperature cycle: Persson et al. [3] have used Dynamic Mechanical Thermal Analysis (DMTA) to study and compare the individual reaction kinetics of commercial adhesives and primers with that of a model rubber compound. They conclude that the reaction sequences of the three components need to be matched in the best possible manner for optimal bonding.

The second condition is the presence of efficient chemisorption and cross-bridging reactions that allow the generation of chemical adhesion at the different interfaces.

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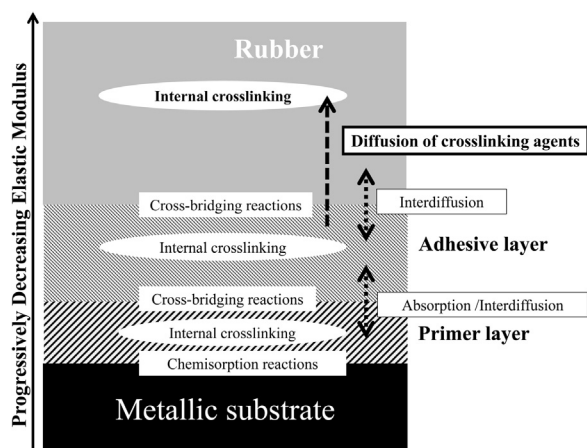
Fig. 1. Reaction and diffusion phenomena in the metal/primer/adhesive/rubber interfacial region during the vulcanization bonding process.

While the efficiency of chemisorption at the metal/primer interface is strongly related to the preparation of the metallic surface (chemical and mechanical treatments) [1], the cross-bridging reactions at the primer/adhesive and adhesive/rubber interfaces are made possible by the diffusion/reptation of polymer chains and the faster diffusion-reaction of the bi-functional crosslinking agents present in the primer and adhesive layers [1]. Although adhesives and primers are generally proprietary products with an undisclosed composition, typical formulations consist of solutions of polymer chains and crosslinking agents in volatile solvents. Typical crosslinking agents are phenolic compounds for the primers and benzoquinone derivatives (such as dinotrosobenzene) for the adhesives [1]. These two kinds of reactive species are able to react with diene rubbers elastomer chains [4], while the polymer chains act as film formers when the solutions are coated on the surface and the solvent evaporated [1], and provide reactive sites for cross-bridging reactions with the polymer/elastomer chains of the adjacent layer.

Last but not least, the third condition to obtain high performance rubber-to-metal adhesion is the generation of a gradually decreasing elastic modulus from the metal substrate to the bulk of the rubber. This implies the development of a very high modulus layer (the thickness is typically about 15–20 μm) in the rubber immediately adjacent to the adhesive [2]. It is assumed that this is made possible by the diffusion of the crosslinking agents contained in the adhesive layer (benzoquinone dioxime derivatives) into the rubber and their reaction with rubber chains. The resulting rubber interphase region has a higher final crosslinking density than the bulk rubber, in which crosslinking is only generated by the reactive agents initially present in the rubber compound.

In the present work, we propose to use a rheological approach in order to study experimentally these phenomena. The reactive interfacial assembly (metal/primer/adhesive/rubber) is reproduced in a simple rotational rheometer with disposable plate-plate geometry. As described by Msakni et al. [5] in the case of dicumyl peroxide diffusion reaction in an ethylene–octene copolymer, such a multilayer setup allows sensing and modelling this key phenomenon. In addition, the same rotational rheometer can be used to separately characterize the individual rheokinetic behavior of the different reactive layers: primer, adhesive and rubber.

2. Materials and methods

2.1. Materials

The commercial primer/adhesive system was provided by the LORD corporation: The adhesive (Chemosil 425) and the primer (Chemosil 211) are thixotropic liquids containing about 25 weight % of solid in volatile solvents. They respectively contain undisclosed benzoquinone dioxime derivatives and a phenolic resin, which makes them are suitable for vulcanization bonding of natural rubber onto aluminum.

Two natural rubber/sulfur compounds were used. As can be seen in Table 1, they only differ by the presence or absence of a sulphur based curing system.

The rheokinetic behavior of the reactive rubber compound was previously characterized and modeled [6],[7]. These earlier studies, which involved the use of a standard Moving Die Rheometer (MDR) [8], provide a reference characterization. In particular, it was shown that for cure temperatures lower than 150 °C, the reversion phenomenon can be neglected [7]. In such a case, the rheokinetic behavior can be described by a simplified version of the Kamal & Sourour model [6]:

$$\frac{d\alpha}{dt} = \left(A_1 exp\left(-\frac{E_1}{RT}\right) + \alpha \times A_2 exp\left(-\frac{E_2}{RT}\right) \right) \times (1 - \alpha)^2 \tag{1}$$

where: A_1, A_2 and $E_1 = E_2$ are kinetic parameters (reported in Table 2) and α is the degree of cure at an isothermal reaction time t defined as :

$$\alpha(t) = \frac{G'(t) - G'_0}{G'_{max} - G'_0} \tag{2}$$

where: $G'(t)$ is the measured dynamic elastic modulus as a function of time, and G'_0, and G'_{max}, the initial and final values, respectively.

2.2. Rheological experiments

A rotational rheometer (HAAKE MARS III, Thermo Fisher Scientific) equipped with a Peltier temperature control

Table 1
Composition of the model rubber compounds.

Component	Parts. (by weight)	
	Reactive rubber	Non-reactive rubber
Rubber gum	100	100
Fillers (including carbon black)	25	25
Plasticizer	5	5
Sulphur based curing system	9	0
Other additives	2	2