Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Test method

Influence of reversion on adhesion in the rubber-to-metal vulcanization-bonding process

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ARTICLE INFO

ABSTRACT

The vulcanization bonding process is used in a growing number of industrial applications where rubber-to-metal bonded assemblies are needed. The complexity of this process lies in the fact that the vulcanization of the rubber and curing of an adhesive previously coated on the metallic surface have to take place simultaneously during a single molding step. In the present work, we present an instrumented molding device allowing the production of adhesion peeling test samples under well controlled curing temperature cycles. Tests performed on a model natural rubber compound with a commercial adhesive system show that, for high cure temperatures, the quality of the rubber-to-metal bonding obtained is significantly reduced. The decrease of the peeling energy appears to be inversely proportional to the reversion undergone by the rubber during cure. Such a result points out the necessity of taking into account this phenomenon for optimization of the vulcanization bonding process.

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1. Introduction

The so-called "vulcanization bonding process" is used for the production of rubber-to-metal bonded assemblies for a wide and growing range of applications, particularly for the reduction of noise and vibration in the automotive industry. This complex process 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 reactive molding step, as opposed to "post-vulcanization bonding" techniques [1]. Although the detailed bonding mechanism remains unknown [1], it is clear that it involves various diffusion phenomena, along with chemisorption and bulk and interfacial crosslinking reactions [2]. In particular, a rubber interphase is formed in the vicinity of the metallic surface due to the diffusion-reaction of crosslinking agents contained in the adhesive layer into the rubber. Typically, these reactive agents are benzoquinone dioxime derivatives [1] able to react with rubber chains, increasing the crosslink density in a rubber layer ranging from 10 to 80 μm [2,3].

Such a complex mechanism makes optimization of the process based on modelling and simulation difficult. Consequently, trial-and-error approaches involving the molding and characterization of normalized adhesion test samples are generally used both in industrial and academic research [4–6].

The quality of the rubber-to-metal adhesion obtained depends on a large number of parameters, ranging from the initial structure and preparation of the metallic surface, the adhesive and rubber compounds used and the thermal history during the vulcanization process [7]. Nevertheless, one key parameter arising from these studies is the

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molding temperature, which was shown to affect the quality of the adhesion between rubber and metal. Of course, it also affects the molding time, and thus the productivity of the process. Nevertheless, while Fernando et al. [4] observe an increase of the adhesion strength for higher cure temperatures, Jeon and Seo [6] observed a degradation of the adhesion when the cure temperature increases. However, in both cases, the authors conclude that temperature mainly influences the formation of the rubber interphase during cure, which in turn affects the adhesion [4,6].

In the present work, we propose to use a mixed approach with, on the one hand, an instrumented molding device allowing the production of adhesion peeling test samples under well controlled curing temperature cycles and, on the other hand, two efficient kinetic models of the rubber cure reaction, allowing prediction of the influence of temperature cure cycles on the bulk state of the rubber. We will show that, for the model sulfur cured natural rubber compound studied, the decrease of adhesion quality at high cure temperature is correlated with the development of the reversion phenomenon affecting crosslink density.

2. Materials and methods

2.1. Materials and kinetic models

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

A model natural rubber/sulfur compound was used (Table 1). The cure kinetics of this system was previously characterized and modeled by our team [8,9]. These earlier studies have shown that, for cure temperatures lower than 150°C, the reversion phenomenon can be neglected [9]. In such a case, the rheokinetic behavior can be described by a simplified version of the Kamal & Sourour model [8] (Equation 1):

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

where: A_1, A_2 and E are kinetic parameters (reported in Table 1) and α is the degree of cure at reaction time t, related to the sulphur crosslink density.

Table 1
Composition of the model rubber compound and kinetic parameters of the models with and without taking into account the reversion phenomenon.

Component	phr	Kinetic model		
		Kinetic model without reversion (Equation 1) [8]	A_1 (s^{-1})	1.7×10^2
			A_2 (s^{-1})	1.0×10^{10}
Natural rubber	100		E (kJ/mol)	92.7
Carbon black	25	Kinetic model with reversion (Equations 2–8) [9]	Av_1 (s^{-1})	9.5×10^2
Oil	5		Av_2 (s^{-1})	6.0×10^9
Zinc oxide	4		Ev (kJ/mol)	91.0
Sulphur	3		X (%)	56
Stearic acid	2		A_r (s^{-1})	1.2×10^{18}
Octamine	2		E_r (kJ/mol)	180

In contrast, for higher temperatures, the reversion phenomenon becomes significant, with a decrease of the final degree of cure α, due to the thermal degradation of a fraction of the sulphur crosslinks, leading to a lower final crosslink density [9]. In such a case, a more complex model is needed to take in order to take into account this phenomenon [9]. The overall reaction can be described by the following scheme (Equations 2 and 3):

$$S \xrightarrow{vulcanisation} XC_1 + (1 - X)C_2 \qquad (2)$$

$$C_2 \xrightarrow{reversion} P \qquad (3)$$
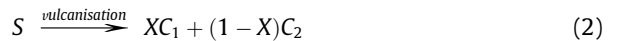
where:

−S represents the sulfur available for the formation of crosslinks
−C_1 and C_2 represent the stable and unstable sulfur crosslinks formed during vulcanization, respectively.
−X is a temperature independent stoichiometric ratio.
−P represents the non-reactive product of the reversion reaction.

The vulcanization reaction (Equation 2) can be described by the same simplified Kamal-Sourour model as above (Equation 4):

$$\frac{d\alpha_v}{dt} = (A_{v1} + \alpha_v \times A_{v2}) \times exp\left(-\frac{E_v}{RT}\right) \times (1 - \alpha_v)^2 \qquad (4)$$

Note that this equation is similar to Equation 1, except that the kinetic parameters Av_1, Av_2 and Ev (reported in Table 1) are slightly different and α_v is a "virtual" degree of cure without reversion. The real degree of cure, α, is obtained by taking into account the reversion reaction (Equation 3), which is considered to be a first order reaction (Equation 5):

$$\frac{d\alpha_2}{dt} = -A_r \times exp\left(-\frac{E_r}{RT}\right) \times \alpha_2 \qquad (5)$$

with:
$$\alpha_1 = X\alpha_v \qquad (6)$$

$$\alpha_2 = (1 - X)\alpha_v \qquad (7)$$

$$\alpha = \alpha_1 + \alpha_2 \qquad (8)$$

The stoichiometric ration X and reversion kinetic parameters E_r and A_r are reported in Table 1. Just as for Equation 1, this more complex model can be solved numerically. In our calculations, we have been using a simple 4th order Runge & Kutta method to calculate the evolution of α with temperature and reaction time.

2.2. Molding and characterization of peeling test samples

2.2.1. Instrumented metallic substrate for rubber bonding

The ISO813 peeling test [10] was chosen since it is widely used in industry for the characterization of