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Assessment of Failures of Nitrile Rubber Vulcanizates Through High-pressure and High-temperature Gas Media: Effect of Zinc Oxide (ZnO) Nanoparticles

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Assessment of Failures of Nitrile Rubber Vulcanizates Through High-pressure and High-temperature Gas Media: Effect of Zinc Oxide (ZnO) Nanoparticles

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Abstract
Most rubber products used in high-pressure and high-temperature gases environment usually suffer from the rapid gas decompression (RGD) failures such as crack, void, bubble, blister, and rupture. Some ingredients of rubber compounding such as zinc oxide (ZnO) as a cure activator can affect on rubber vulcanizates properties and durability. The RGD resistance of nitrile (NBR) rubber vulcanizates using zinc oxide nanoparticles (nano-ZnO) were investigated compared to those of NBR with conventional rubber grade (CRG) ZnO. Results showed that the by applying nano-ZnO in NBR compounding formulations, higher corsslink density and hardness and lower tensile strength were obtained in comparison with the CRG-ZnO ones. However, the RGD resistance was lower in nano-ZnO containing compounds of NBR than CRG-ZnO ones. In addition, all NBR compounding formulations in both systems were passed the RGD test. Application of nano-ZnO particles might be more suitable in practical conditions than CRG-ZnO curing agent system, since higher physico-mechanical properties and good RGD resistance were required, simultaneously.

Keywords: RGD resistance, Zinc oxide, Nanoparticle, Crosslink density, Nitrile rubber.

Introduction
The rapid gas decompression (RGD),commonly known as explosive decompression (ED) is the phenomenon which high-performance elastomers such as NBR components are exposed to gases at high pressure for a long time [1]. In this conditions, gas molecules are penetrated into the elastomer. When the external pressure applied to the rubber quickly released, creation of pressure gradient and traped gas molecules in the elastomer may create the different damages such as various internal and external cracks, voids, bubble, and surface blisters [2]. Different standards have been developed to evaluate the performance of elastomers against RGD procees, which the most accessible are ISO 23936-2:2011[1]. A study of influencing testing parameters on RGD resistance of elastomer was investiged by Schrittesser and et al. [3], and it seems that the study of the effect of rubber compound formulation on RGD resistance of elastomer is a controversial issue. Developing nanoscale fillers and activators has been an attractive approach to enhance and achieving desired properties of polymers. In this regard, different nanoscale fillers such as silica, montmorillonite, and aluminum oxide have been used

in previous research [4]. Zinc oxide is widely used as an important inorganic activator in sulfur vulcanization of unsaturated elastomer in rubber industry. Conventional rubber grade ZnO (CRG-ZnO) and nano-ZnO own the same chemical composition, except the nano-ZnO have many fantastic characters, e.g. “little size effect”, “surface effect,” and “quantum effect” [5]. The use of nano-ZnO has been recently considered due to the specific physical and mechanical properties, including chemical and thermal stability, low dielectric constant, and high catalysis activity [6].Li et al. [7] reported that adding nano-ZnO in natural rubber can greatly reduce the content of ZnO. When using 0.8 phr nano-ZnO the mechanical properties of NR vulcanized were same or better than that of 5 phr of CRG-ZnO, which has main effect on decreasing some adverse environmental of ZnO. So far, many studies have been done on the effect of zinc oxide nanoparticles on mechanical, physical, and thermal aging of elastomers [8,9].

Since the effect of ZnO nanoparticles on RGD resistance of rubbers have not been investigated yet, The present study is focused on the effect of nano-ZnO as curing activator in NBR vulcanized on RGD resistance and the results are compared with conventional rubber grade (CRG) ZnO.

Experimental

Materials and Mixing

For this investigation, 100 phr acrylonitrile-butadiene rubber (NBR, %35 Acrylonitrile, 35 L KNB, Kumho) were used. Compounding ingredients, 50 phr carbon black (HAF-N330) from Pars carbon Ltd. Iran, 1-5 phr nano-ZnO (with %99.8 purity and 20 nm average particle size) from US nano material and 1-5 phr CRG-ZnO (with %99 purity) from Pars Shimi co. Iran, 1 phr sulfur (SU95) from Struktol company, 0.5 phr TMTD and 1.5 phr CBS, 1 phr IPPD, 1 phr Stearic acid, and 5 phr DOP oil were of commerical grade. The compounds were prepared using a laboratory mixing two-roll mill in accordance with ASTM D3182.

Rubber vulcaniztes properties

The cure characteristics were measured at 160 ^{o}C using a moving die rheometer (MDR). The vulcanization process was carried out at 160 ^{o}C for the pre-determined optimum cure time from MDR rheometer in an electrically heated hydraulic press (Santam Co., Iran) under a pressure of about 160 bar. For measurement of the crosslink density, about 0.5 g of NBR vulcanizates were immersed in 10 ml of the toluene solvent for 72 h at room temperature according to ASTM D6814. Then dried in an oven at 70 ^{0}C for 20h. the Crosslink density was calculated using Flory–Rehner equation [10]. The tensile strength were determined at room temperature using tensile test machine (STM-20, Santam Co. Iran) based on ASTM D412. The hardness was measured by cylindrical sampeles (with 12.5±0.5 thick and 29±0.5 mm in diameter) with shore A durometer hardness tester according to ASTM D2240.

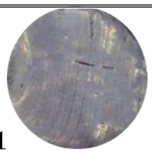
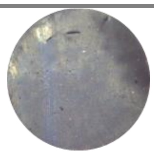
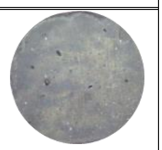
Rapid Gas Decompression (RGD) test

In order to evalute the RGD resistance of NBR vulcanized, O-ring samples with a nominal CSD of 5.33 mm were subjected to the RGD test similar to ISO 23936-2 standard. Details of RGD test rig and related testing conditions were published in our previous studies [11].

Results and discussion

For the investigation of the influence of ZnO nanoparticles on the RGD resistance, high-integrity NBR O-rings (without almost any blister, crack, and void) vulcanized by nano-ZnO and CRG-ZnO were subjected to the RGD test. The performance of O-rings by 16-X magnification loop is summarised in Table 1. Examination of Damages of four O-rings of each compound was performed, one of them is presented as an example and its RGD rating is highlighted.it was noted that by increasing the amount of ZnO, more cracks were appeared in compounds containing CRG and nano-ZnO, with the difference that in vulcanized including nanoparticles, the maximum length of the cracks was seen in content of 3 phr. However, based on the standard evaluation the compound with 3 phr nano-ZnO also has the acceptable RGD resistance rating. This RGD resistance trend can be attributed to properties such as crosslink density, hardness and tensile strength.

Table 1: RGD resistance ratings of NBR vulcanized containing CRG and nano-ZnO.

5phr	4phr	3phr	2phr	1phr	**Content**	
 1	 **1**	 **1**	 **1**	 **1**	**After RGD**	**CRG-ZnO**
 1	 **1**	 **3**	 **1**	 **1**		**Nano-ZnO**

By increasing the content of ZnO, more accelerators and sulfur are activated during vulanization process, and increasing the torque difference (ΔM) shown in Table 2 could be used as an indirect indication of crosslink formation. crosslink density of NBR vulcanized by ZnO nanoparticles due to having the more uniformly dispersed in rubber matrix and higher specific surface of nanoparticles was higher than compounds containing CRG-ZnO. It is noteworthy that in content of 4 and 5 phr nano-ZnO, the crosslink density has been reduced due to the agglomeration of fine nanoparticles [11].

Table 1: The cure characteristics of NBR compound with nano-ZnO and CRG-ZnO

Compound	Nano-1	Nano-2	Nano-3	Nano-4	Nano-5	CRG-1	CRG-2	CRG-3	CRG-4	CRG-5
ΔM (dN.m)	13.54	14.96	16.25	14.63	16.18	12.90	13.66	14.09	14.31	14.93

In Fig.2 the changes of tensile strength of rubber compounds with different content of nano-ZnO and CRG-ZnO are shown. Increasing of crosslink density caused by raising the amount of ZnO can improve distribution of external stress and then led to increase of tensile strength. As shown in Fig. 2, With the further increase of crosslink density, creation of stress concentration has reduced tensile strength.

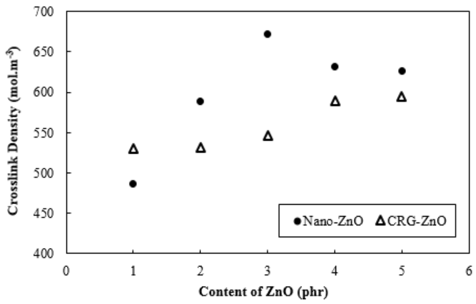


Figure 1: Effect of type of ZnO (Nano and CRG) on crosslink density of NBR vulcanized.

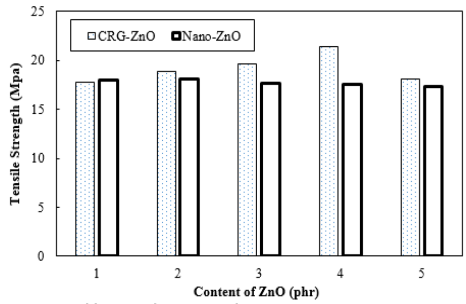


Figure 2: Effect of type of ZnO (Nano and CRG) on tensile strength of NBR vulcanized.

Application of nano-ZnO results in increment of crosslink density and hardness, and reduction of the tensile strength has led to lower of RGD resistance of NBR vulcanized. Because of by increasing the crosslink density and hardness, the elastomer network resists the relaese of gas molecules during and after decompression event and trapped gases in the chains of rubber cause the damages such as cracks and voids. On the other hand, reduction in tensile strength Accelerates the crack initiation and growth.

Conclusions
The present work set out to study the effect of nano-ZnO on RGD resistance of NBR rubber compounds. ZnO nanoparticles were dispersed more homogeneously in NBR matrix and specific surface area over CRG-ZnO at the same mixing condition. For this reason, it has created more crosslink density in the NBR network and less tensile strength. The increased crosslink density led to greater damage in RGD process. Based on results, by increasing crosslink density and reducing tensile strength of nano-ZnO sysetm, the RGD resistance of NBR vulcanized was decreased. Because of dissolved gas enters the elastomer cannot dissolve out rapidly and cracks created earlier during decompression step, respectively. Eventually, despite the lower RGD resistance of NBR vulcanized by nano-ZnO, all compounds were passed the RGD test, and can be used in operating conditions that require high hardness and high crosslink density NBR compounds.

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