ABSTRACT: Zinc methacrylate (ZMA) was incorporated into ethylene-propylene diene rubber (EPDM) by direct mixing of the metal salt with the rubber or was in-situ prepared in the rubber matrix through neutralization reaction of zinc oxide (ZnO) and methacrylic acid (MAA). Tensile and tear tests showed that ZMA had a great reinforcing effect for the EPDM. It was also found that ZMA reinforced EPDM vulcanizates can retain their mechanical properties under thermo-oxidative aging. Moreover, the incorporation of ZMA induces a substantial improvement in the adhesive strength of the EPDM onto aluminum substrate. The reinforcing effect and an enhancement in adhesion was greatly manifested when the ZMA is in-situ formed with an excess amount of ZnO. The extraordinary improvement in the properties is supposed to be related with the formation of ionic crosslink as well as the degree of dispersion of ZMA domain in the rubber matrix.

Keywords: EPDM, ZMA, hybrid composite, ionic crosslink
I. Introduction

A metallic (zinc, magnesium, or sodium) salt of methacrylic acid has been known to be as an effective coagent for peroxide curing of rubbers due to their positive contribution to the performance of unsaturated and saturated elastomers.\(^1\) It has been found that crosslink structure of the rubber containing the metallic salt consists of chemical crosslink (covalent crosslink) as well as physical crosslink (ionic crosslink), which is formed via homopolymerization and graft copolymerization of metallic methacrylate onto the rubber backbone.\(^2,4\) The crosslink structure of the rubber vulcanized by peroxide in the presence of zinc methacrylate is demonstrated in Figure 1. It has been reported that there is a great improvement in tensile strength, abrasion resistance and hardness with excellent resilience in rubber vulcanizates such as styrene-butadiene rubber(SBR),\(^5\) nitrile rubber(NBR),\(^6,6\) ethylene-propylene diene rubber(EPDM),\(^7\) hydrogenated nitrile rubber(HNBR),\(^8,9\) and ethylene vinylacetate copolymer(EVM)\(^10\) when divalent(zinc or magnesium) or monovalent(sodium) metallic coagents are incorporated. As compared to conventional reinforcing fillers such as silica and carbon black, reinforcement by the use of the metallic coagents has several benefits in that they provide an optical transparency to the vulcanize and do not induce any processing difficulties during mixing process as well. Rubber vulcanizates with low surface energy could also be fabricated when the fluoroalkyl unsaturated carboxylic acids were used together with the metallic salts of methacrylic or acrylic acids.\(^11,12\)

Direct adhesion between rubber and metal during curing is important matter of interest for the production of valve sensors, packings, and rubber vibration insulators consisting of combinations of metals and rubber vulcanizates.\(^13,14\) These devices require strong adhesion between rubbers and metals. The rubber-metal adhesion can be achieved using certain adhesives, which lead to additional costs and environmental pollution. In this study, we aim to examine the effect of incorporation of zinc methacrylate into EPDM on the mechanical properties, stability for thermal ageing and adhesive properties onto a metallic substrate of the rubber.

II. Experimental

EPDM (KEP-350, ENB type, ML1+4 (at 100 °C) = 83) was supplied by Kumho E. P., Korea. ZMA, MAA, and ZnO were purchased from Aldrich, and were used as received. EPDM/ZMA composites were prepared by (1) in-situ formation of ZMA via mixing the rubber with MAA and ZnO, and (2) direct melt mixing of the ZMA with the rubber, and a subsequent curing of the mixtures. Mixture of EPDM and a metallic coagent was prepared in a HAKKE internal mixer at the rotor speed of 35 rpm and the initial temperature 45 °C, followed by the addition of the peroxide on the two-roll mill. Vulcanization was conducted using a Carver hot press at 170 °C for 10 min, and cut into specimens for measurement of the mechanical properties.

Tensile tests were carried out using a universal testing machine (United Co., STM-10E) at 30 °C using a crosshead speed of 500 mm/min according to ASTM D412 specifications. Tear strength was measured as per ASTM D624 using unnicked 90° angle test pieces (die C) at 30 °C at a crosshead speed of 500 mm/min.

A rubber-to-metal adhesion was measured using 180° peel test. Aluminum foil was cut to 150 mm × 150 mm sizes and cleaned with acetone. 3 g of