

Preparation and Properties of EPDM/Zinc Methacrylate Hybrid Composites

Jong-Hoon Won, Hyun-Seok Joo, and Young-Wook Chang[†]

Dept. of Chemical Engineering, Hanyang University, Ansan 426-791, Korea

(Received January 18, 2005, Revised and Accepted February 24, 2005)

에틸렌 프로필렌 디엔 고무/메타크릴산아연 하이브리드 복합체의 제조와 물성에 관한 연구

원 종 훈 · 주 현 석 · 장 영 옥[†]

한양대학교 화학공학과

(2005년 1월 18일 접수, 수정 및 채택 2005년 2월 24일)

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.

요 약 : 메타크릴산의 아연염인 ZMA를 EPDM고무와 직접 블렌딩하거나 또는 ZnO와 MAA의 형태로 첨가한 후 이들간의 중화반응을 유도하여 고무에 in-situ로 형성시키는 방법을 이용하여 EPDM/ZMA 복합체를 제조하였다. 인장시험, 인열시험, 열노화시험 결과 ZMA의 첨가는 EPDM의 기계적 물성 및 열노화에 대한 안정성을 현저히 향상시킬 수 있음을 알 수 있었다. 또한, ZMA의 첨가는 EPDM고무와 금속과의 접착력을 크게 향상시킬 수 있음을 알 수 있었다. 이러한 기계적물성 및 접착물성의 향상효과는 과량의 ZnO를 사용한 중화반응에 의해 ZMA를 형성시킨 복합체에서 더욱 크게 나타났다. 이는 ZMA의 도입에 의한 이온가교결합의 형성 및 고무매트릭스에서의 ZMA 도메인의 분산도와 연관되는 것으로 판단되었다.

Keywords : EPDM, ZMA, hybrid composite, ionic crosslink

[†] 대표저자(e-mail : ywchang@hanyang.ac.kr)

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),^{3,6} 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 vulcanizate 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

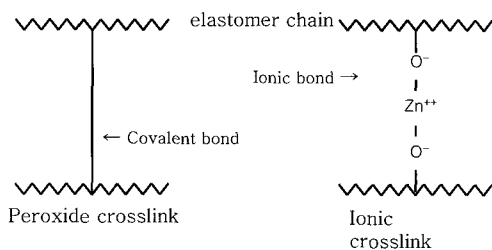


Figure 1. Schematic diagram of cross-linking structure of peroxide cured elastomer vulcanizate containing zinc methacrylate.

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

the rubber mixture was placed between the two aluminum foils in such a way that part of the foil was not covered with polymeric material, and the assembly was vulcanized in a hydraulic press at 170 °C. Thickness of the adhesive layer was about 0.12 mm, and the dimensions of the test specimen were 100 mm × 24 mm, of which the bonded area was 50 mm × 24 mm. Care was taken to keep the thickness of the adhesive uniform in all the joints. The 180° peel strength of the joint was determined using universal testing machine at 30 °C. A steady load was applied at a rate of 500 mm/min until separation was complete. The average peel strength (kN/m) was determined from the load as follows:

$$\text{Peel strength} = F / w$$

where F is the average force in Newtons and w is the width of the specimen.

III. Results and Discussion

Figure 2 presents dependence of ZMA contents in the rubber on tensile properties of the vulcanizates. Assuming that ZnO and MAA would totally react into ZMA, amount of ZMA that could be obtained was used to represent the content of ZnO/MAA used. As can be seen in the Figure 2(a) to (c), with increasing amount of ZMA, tensile strength and modulus at a given strain increases dramatically. This dramatic reinforcing effect, even without the presence of conventional reinforcing fillers such as carbon black or silica, is attributed to the zinc salt linkage which was generated via a

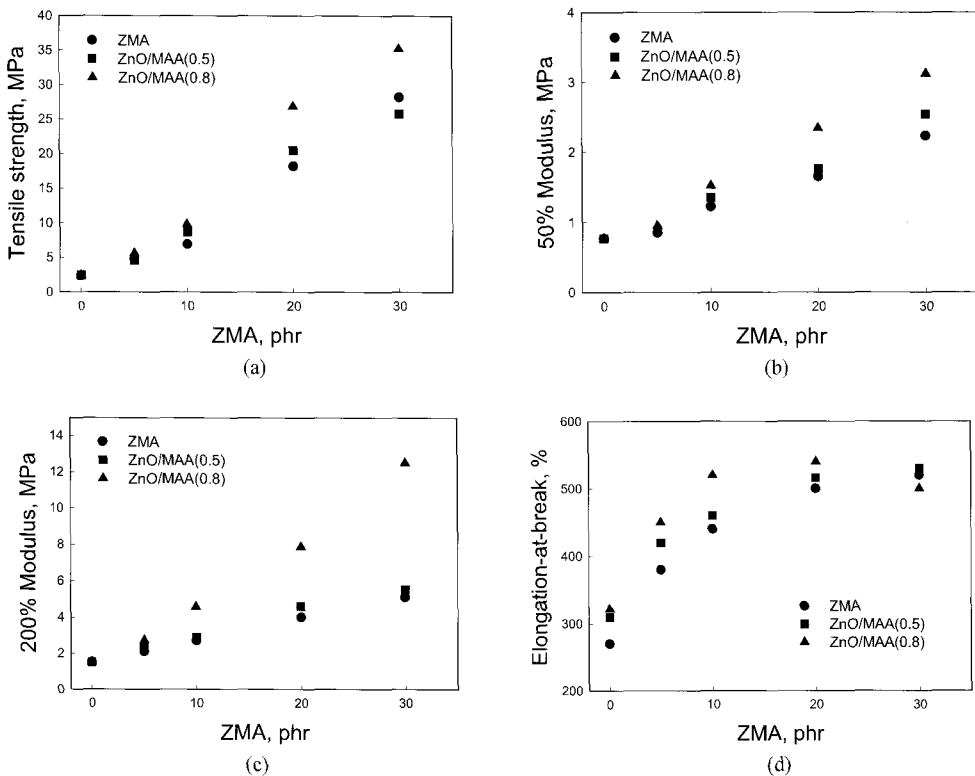


Figure 2. Effects of ZMA content on tensile properties of the EPDM vulcanizates: (a) ZMA content vs. tensile strength; (b) ZMA content vs. 50% modulus; (c) ZMA content vs. 200% modulus; (d) ZMA content vs. elongation-at-break.

graft copolymerization of poly-ZMA onto the rubber backbone during vulcanization.²⁻⁴ Salt crosslink increase with the increase of ZMA content in the rubber. It is well known that vulcanizates containing ionic crosslinks have good mechanical properties, which was caused by slippage of the chains during deformation and a consequent energy dissipation.^{15,16}

Figure 2 also demonstrates that the reinforcing effect is greater when the ZMA is formed in-situ as compared to the case when the ZMA is added directly into the rubber as far as the ZnO is used excess to the MAA. It is supposed that ZnO and MAA would react to form ZMA more efficiently when the ZnO is used in excess. When molar ratio of ZnO to MAA is 0.8 and the in-situ formed ZMA content is 30 phr, there are almost one order of magnitude increase in the tensile strength without any significant loss in extensibility. The effect of the ratio of ZnO to MAA on the mechanical properties was also observed by other researchers.^{5-8,10} In the case of HNBR and NBR reinforced by in-situ prepared ZMA, better reinforcement was obtained when ZnO was in excess over MAA and the optimal mole ratio of ZnO to MAA was about 0.6–0.8.^{3,6,8,9} Studies on electron micrograph of the composites showed that the ZMA domain is dispersed uniformly in a rubber matrix at a nanometer scale, and the dispersion of ZMA is much finer when the ZMA was in-situ formed as compared with the case when the ZMA is added directly into the rubber. The finer dispersion of the ZMA causes a huge increase of the interfacial area between the metallic salts and matrix polymer, and thereby a remarkable increase in the mechanical properties was obtained. Figure 2(d) presents the variation of tensile strain with ZMA content. The ultimate strain increases with the content of ZMA and become constant when the ZMA content exceeds 20 phr.

Figure 3 shows the variation of tear strength, a measure of resistance to crack propagation, of the EPDM/ZMA composites with the amount of ZMA loading. As seen in tensile strength, the tear strength

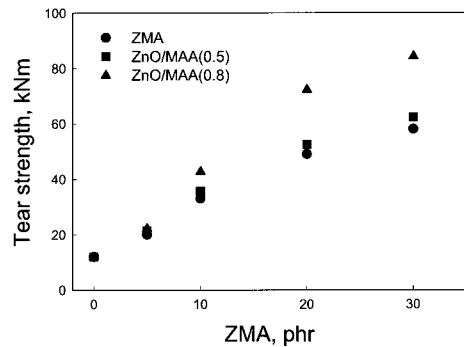


Figure 3. Effects of ZMA content on tear strength of the EPDM vulcanizates.

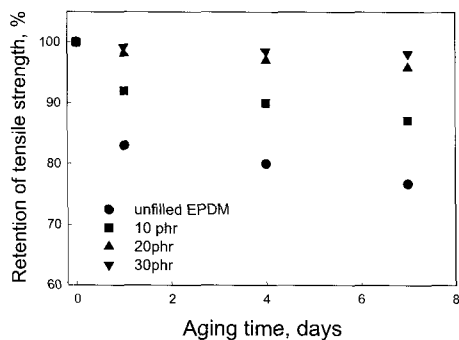
increases with the increase in the amount of ZMA content. And, the composites containing in-situ formed ZMA (ZnO/MAA = 0.8) exhibits a highest tear strength. The uniformly dispersed salt crosslinks in the rubber matrix is considered to dissipate energy concentrated at the tip of the growing crack, which lead to the increase in the resistance to tearing. These observations indicate that the uniform dispersion of salt crosslinks in the rubber matrix can offer the composite effective enhancement in toughness and strength as well as stiffness.

Effects of the salt crosslink on the strength can be investigated via a swelling of the rubber vulcanizate in propanone/HCl mixed solvent for 2 days, which causes destruction of the salt aggregation. Tensile and tear measurements using a swollen specimen after vacuum drying showed that strength of the rubber decreased markedly, which is presented in Table 1. This implies that the high strength of EPDM/ZMA vulcanizates is originated from the salt crosslink.

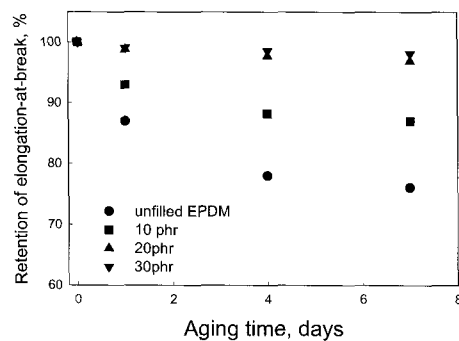
The rubber vulcanizates were subjected to thermal aging at 150 °C for various periods. The retained values of tensile strength and elongation-at-break were calculated and plotted against the ageing time as demonstrated in Figure 4. It is observed that vulcanizates containing ZMA retain tensile strength as well as elongation-at-break to higher values after thermal ageing, being compared with the unfilled EPDM vulcanizate. Increase in the heat aged stabi-

Table 1. Change of Mechanical Properties of EPDM/ZMA Vulcanizate with Acid Treatment (ZMA 30 phr, ZnO/MAA=0.8)

	50% Modulus (MPa)	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation-at-Break (%)	Tear Strength (kN · m)
Before acid treatment	3.2	12.3	36.2	552	86.2
After acid treatment	1.08	2.06	2.75	426	16.8



(a)

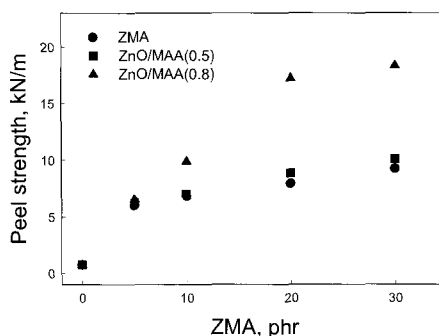
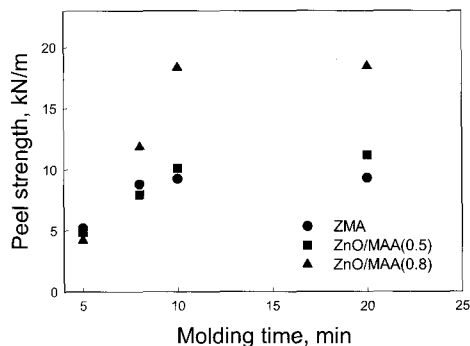


(b)

Figure 4. Effects of thermo-oxidative aging on tensile properties of EPDM/ZMA vulcanizates. (a) Retention of tensile strength vs. aging time; (b) Retention of elongation-at-break vs. aging time.

lity can be observed as the increase in ZMA content in the rubber. Such an enhancement in the thermal stability of the EPDM vulcanizate containing ZMA is supposed to be due to the increase in the salt crosslink which has good heat aged stability.

Figure 5 shows the effect of ZMA on the peel strength of the EPDM onto aluminum substrate. It can be seen that EPDM without ZMA has very low level of adhesion onto metal due to nonpolar nature

**Figure 5.** Effects of ZMA contents on peel strength of adhesive joints.**Figure 6.** Effect of molding time on peel strength of adhesive joints.

of the EPDM. On the addition of ZMA into EPDM, rubber-to-metal adhesion increases substantially when the rubber adhesive is peroxide cured. And, the increase in the adhesive strength is more significant when the ZMA is formed in-situ during vulcanization. This result shows that direct adhesion of rubber onto metal during curing can be achieved without the use of any adhesives. We believe that the enhancement in the rubber-to-metal bonding on

the addition of the ZMA into the rubber is due to the specific interaction of the ionic sites of the rubber with the metal surface. Finer dispersion of ZMA should result in an increase the number of the interactions between the rubber and the metal substrate. This is the reason why the rubber vulcanizate containing in-situ formed ZMA presents a higher adhesive strength than that containing directly added ZMA. Effect of molding time (curing time) on the adhesive strength of EPDM/ZMA (ZnO/MAA=0.8) is presented in Figure 6. As molding time increases, adhesive strength increases. But, when the specimen is cured longer than 10 min, enhancement in the adhesive strength levels off. When the peel strength exceeds 10 kN/m, stick-slip failure mode becomes more predominant in the failure of the adhesive joints and the cohesive failure in the rubber phase was observed.

IV. Conclusion

Addition of ZMA into EPDM can produce a great improvement of tensile and tear strength of the rubber when it is peroxide cured. The increase in the strength is attributed to salt crosslinks generated during curing. In-situ prepared ZMA via a neutralization reaction of ZnO and MAA with an excess amount of ZnO induced a much higher reinforcement than the directly added ZMA. The ZMA reinforced EPDM can retain mechanical properties under thermo-oxidative ageing conditions. Adhesive strength of Al/EPDM joint increases on the addition of ZMA into the rubber, and the enhancement is more significant when the ZMA is formed in-situ in the matrix rubber.

References

1. R. Costin, W. Nagel, and R. Ekwall, "New Metallic Coagents for Curing Elastomers", *Rubber Chem. Technol.*, **64**, 152 (1991).
2. S. J. Oh and J. L. Koenig, "Studies of Peroxide Curing of Polybutadiene/Zinc Diacrylate Blends by Fast FT-IR Imaging", *Rubber Chem. Technol.*, **72**, 334 (1999).
3. X. Yuan, Z. Peng, Y. Zhang, and Y. Zhang, "The Properties and Structure of Peroxide-cured NBR Containing Magnesium Methacrylate", *Polymers & Polymer Composites*, **7**(6), 431 (1999).
4. Y. Lu, L. Liu, D. Shen, C. Yang, and L. Zhang, "Infrared Study on In-Situ Polymerization of Zinc Dimethacrylate in Poly((-octylene-co-ethylene) Elastomer)", *Polym. Int.*, **53**, 802 (2004).
5. D. Yin, Y. Zhang, Y. Zhang, Z. Peng, Y. Fan, and K. Sun, "Reinforcement of Peroxide Cured Styrene-Butadiene Rubber Vulcanizates by Methacrylic Acid and Magnesium Oxide", *J. Appl. Polym. Sci.*, **85**, 2677 (2002).
6. X. Yuan, Z. Peng, and Y. Zhang, "In-Situ Preparation of Zinc Salts of Unsaturated Carboxylic Acids to Reinforce NBR", *J. Appl. Polym. Sci.*, **77**, 2740 (2000).
7. Z. Peng, X. Liang, Y. Zhang, and Y. Zhang, "Reinforcement of EPDM by In-Situ Prepared Zinc Dimethacrylate", *J. Appl. Polym. Sci.*, **84**, 1339 (2002).
8. Y. Saito, A. Fujino, and A. Ikeda, "High Strength Elastomers of Hydrogenated NBR Containing Zinc Oxide and Methacrylic Acid", *SAE Tech. Paper*, *SAE 890359*, 13 (1989).
9. N. Nagata, T. Sato, T. Fujii, and Y. Saito, "Structure and Mechanical Properties of Hydrogenated NBR/Zinc Dimethacrylate Vulcanizates", *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, **53**, 103 (1994).
10. A. Du, Z. Peng, Y. Zhang, and Y. Zhang, "Properties of EVM Vulcanizates Reinforced by In-Situ Prepared Sodium Methacrylate", *J. Appl. Polym. Sci.*, **89**, 2192 (2003).
11. T. Ikeda, B. Yamada, M. Tsuji, and S. Sakurai, "In-Situ Copolymerization Behavior of Zinc Dimethacrylate and 2-(N-ethylper fluorooctanesulphonamido)ethyl acrylate in Hydrogenated Nitrile-Butadiene Rubber during Peroxide Crosslinking," *Polym. Int.*, **48**, 446 (1999).
12. T. Ikeda and B. Yamada, "Copolymerization of Zinc Dimethacrylate and Perfluoroalkyl Acrylates in Different Solvents", *J. Appl. Polym. Sci.*, **71**, 1499 (1999).
13. K. Mori, H. Hirahara, and Y. Oishi, "Direct

- Adhesion between Electroless Nickel Plated Metals and NBR Compounds during Curing”, *Rubber Chem. Technol.*, **70**, 211 (1997).
14. R. Costin and W. Nagel, “Techniques for Bonding Rubber to Metal using Metallic Coagents”, *Rubber World*, **219**(2), 18 (1998).
 15. L. Ibarra and M. Alzoriz, “Vulcanization of Carboxylated Nitrile Rubber by Zinc Peroxide”, *Polym. Int.*, **48**, 580 (1999).
 16. L. Ibarra and M. Alzoriz, “Ionic Elastomers Based on Carboxylated Nitrile Rubber and Zinc Peroxide: Influence of Carboxylic Group Content on Properties”, *J. Appl. Polym. Sci.*, **84**, 605 (2002).