

Reinforcement of SBR/waste rubber powder vulcanizate with in situ generated zinc dimethacrylate

X P Wang¹, B K Cheng, X Zhang and D M Jia

School of Materials Science and Engineering, South China University of Technology, Guangzhou, Guangdong, 510641, China

E-mail: wangxp@scut.edu.cn

Abstract. Methyl acrylic acid/zinc oxide (MAA/ZnO) was introduced to modify styrene-butadiene rubber/waste rubber powder (SBR/WRP) composites by blending. The enhanced mechanical properties and processing ability were presumably originated from improved compatibility and interfacial interaction between WRP and the SBR matrix by the in situ polymerization of zinc dimethacrylate (ZDMA). A refined interface of the modified SBR/WRP composite was observed by scanning electron microscopy. The formation of ZDMA significantly increased the ionic bond content in the vulcanizate, resulting in exceptional mechanical performance. The comprehensive mechanical properties including tensile strength, tear strength and dynamic heat-building performance reached optimum values with 16 phr MAA.

1. Introduction

Waste rubber products are the second largest waste polymer material, following waste plastics. Waste rubber products primarily consist of destroyed tires, rubber shoes and belts, sheets of sealing rubber, etc., which exhibit a solid network structure that makes them undissolved and decomposed before melt. The disposal of waste rubber has become a major environmental issue worldwide. Waste rubber powder (WRP) prepared by grinding could be served as a filler or substitute for rubber makes recycling processes for the material of great importance [1-5]. The development of an environmentally friendly means of waste rubber disposal will help prevent environmental pollution.

However, the incompatibility between WRP and polymer matrices caused by its dense crosslinked network structure and the inert surface of WRP makes the adding of WRP in a raw rubber often disrupt the properties of the mixture.

Unsaturated carboxylic acid salts such as methyl methacrylate acrylic acid zinc, magnesium, etc. produced by the reaction between unsaturated carboxylic acid and metal oxide, hydroxide or carbonate reaction proceeds, can be made by "in situ" preparation in a polymer matrix [6]. Since zinc dimethacrylate (ZDMA) reinforced by hydrogenated nitrile rubber (HNBR) which demonstrates enhanced tensile strength and excellent abrasion resistance was developed by Zeon Chemicals to produce golf balls, unsaturated carboxylic acid salts have been widely investigated as a means of rubber reinforcement by applying unsaturated carboxylic acid and metal oxides directly to the rubber matrix. The in situ generation of unsaturated carboxylic acid salt can be obtained during the mixing and vulcanization process [7-8]. Unsaturated carboxylic acid salt contains a large number of positive and negative ions, which gather together to form an ionic cluster as a result of electrostatic attraction, resulting in the reinforcement of the material. Moreover, the unsaturated groups in unsaturated



carboxylic acid salt can copolymerize with one another as well as undergo a grafting reaction with the polymer matrix to enhance the rubber material [9-10]. The micron-scale dispersion of residual ZDMA particles and the nanoscale dispersion of poly-ZDMA aggregates was observed in the vulcanizates [11].

In this paper, methyl acrylic acid and zinc oxide (MAA/ZnO) were incorporated into styrene butadiene rubber/waste rubber powder (SBR/WRP) composites to increase the compatibleness of the rubber matrix and WRP as well as to subsequently reinforce the composites. The mechanical properties such as wear resistance and fatigue properties were investigated to verify the in situ reinforcement of ZDMA in the rubber matrix. The crosslinking density, processability of the vulcanizate, mechanical and dynamic mechanical properties, dynamic compression fatigue of the sample were measured and analyzed. Scanning electron microscopy (SEM) was used to observe the microstructure.

2. Experimental

2.1. Materials

Methyl acrylic acid (MAA) and zinc oxide (ZnO) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. The WRP used in this research was offered by Guangzhou Aiqi technical Company. The mean particle diameter was 1000 mesh. SBR 1502 was purchased from China Sonipac Cro. The utilized ingredients of the composite including accelerator 2,2-dibenzothiazolesulfide (DM), accelerator N-cyclohexyl-2-benzothiazolesulfenamide (CZ), and activator stearic acid (St) were bought commercially. Carbon black N234 was provided by Shanghai Cabot Chemical Co., Ltd. The fumed silica was supplied by Guangzhou Hongchuang Trading Co., Ltd. Pure dicumyl peroxide (DCP), was purchased from Aladdin Reagent Co., Ltd.

2.2. Sample preparation

The rubber compounds was mixing by a two-roll mill, and the recipe was listed in table 1. Raw SBR was masticated with WRP to obtain a masterbatch, into which various contents of MAA and ZnO were mixed. The proportion of MAA was 0, 4, 8, 12, 16, and 20 phr, respectively. The ratio of MAA to ZnO was fixed in 2.1:1 (wt%:wt%) and other additives were loaded subsequently. The time and roller temperature for mixing was 10 minutes and 50°C respectively. The compound rubber was placed one night before vulcanization. Thenceforth, the samples were vulcanized at 150°C under a pressure of 10MPa for top optimum cure time T_{90} , which was measured by the UCAN UR-2030 vulcameter (Taipei, Taiwan). Kinds of vulcanized specimens were prepared for tensile angle tear and compress tests, respectively.

Table 1. SBR/WRP/filler composite contents.

Ingredient	SBR	RP	MAA	ZnO	St	N234	DCP
phr	100	10	0~20	0~9.5	2	34	2

2.3. Measurements

Tensile properties and tear strength were investigated according to ASTM D412 and ASTM D3185, respectively, on an Electron Omnipotence Experiment Machine U-CAN UT-2060 (Taipei, Taiwan) instrument with a strain rate of 500 mm/min according to standard descriptions. Dynamic mechanical analysis (DMA) spectras of modified and unmodified SBR/WRP composites were acquired by using a DMA243 dynamic mechanical spectrometer (Nestel, Germany) , on the tensile mode with 0.5% strain and 10 Hz frequency. The surface morphologies of the metal-sprayed samples were observed by SEM, Quanta 200 (FEI, Netherlands).

A crosslinking density test was conducted by swelling experiments. Weighted samples were immersed in toluene to achieve balance. The crosslinking density (n) was calculated from volume fraction of the rubber (V_r) in a swollen sample. The values of V_r and n were attained from the equations provided by Valentín and Nie [12-13], as follows:

$$V_r = \frac{\frac{w_2 - f_{ins} w_0}{\rho_2}}{\frac{w_2 - f_{ins} w_0}{\rho_2} + \frac{w_1 - w_2}{\rho_1}} \quad (1)$$

$$-[\ln(1 - V_r) + V_r + \chi V_r^2] = V_0 n (V_r^{1/2} - \frac{V_r}{2}) \quad (2)$$

where w_0 is the weight of dry sample originally; w_1 and w_2 represent the weights of the swollen samples and the unswollen samples, respectively; f_{ins} is the weight fraction of the components which was undissolved in toluene solvent; ρ_1 and ρ_2 are the densities of the solvent and the rubber, respectively; the Flory-Huggins polymer-solvent interaction term is represented as χ , which is assumed to be $0.29 + 0.90V_r$ for SBR and the toluene pair at 25°C ; the toluene molar volume $V_0 = 106.2$ ml/mol. In our experiment, samples were immersed in toluene solvent for seven days at 25°C . Then, w_1 was determined from the surface-cleaned swollen rubber, and w_2 was determined as the constant weight of the swollen sample after being dried for five hours at 80°C . Accordingly, V_r and n can be obtained through equation (1) and (2). For measuring the ionic and covalent crosslink density separately, the samples were previously swelled in a mixed solvent of acetone/hydrochloric acid for three days at 60°C to destroy the ionic network, and then immersing in toluene for seven days. The total crosslink density is a combination of the ionic crosslink density and the covalent crosslink density.

3. Results and discussion

3.1. Microstructure of the SBR/WRP blends

The microstructure of SBR/WRP and MAA/ZnO modified SBR/WRP were investigated by SEM at a magnification of 500X; results are depicted in Figure 1. The SEM micrographs show that the brittle fracture surface of the modified SBR/WRP is different from that of SBR/WRP. Hole formation as a result of the detachment of WRP from the SBR matrix can be seen in the micrographs, in which it can be seen that the MAA/ZnO modified SBR/WRP in figure 1(b) demonstrates more irregular fine shapes and a rough surface as compared to the SBR/WRP sample depicted in figure 1(a). This pattern indicates the well distribution of WRP in the rubber matrix and strong interfacial actions between the WRP and rubber matrix after modification. The improved bonding at the interface of the composite materials and the rubber powder dispersed in the matrix can be ascribed to the in situ generation of ZDMA by the reaction of ZnO and MAA, and by the grafting of MAA to the rubber matrix during the mixing and curing process. This is demonstrated by the increased hardness and maximum torque of the sample.

The effective wetting of WRP by the matrix and strong interfacial interactions are required in order to obtain an SBR/WRP compound with satisfactory mechanical properties and well distribution of WRP in the rubber matrix.

3.2. Vulcanization characteristics, mechanical properties and crosslink density of SBR/WRP compounds

As shown in table 2, increasing the rubber powder loading in SBR compounds reduces the optimum cure time T_{90} in the presence of unreacted accelerators in the rubber powder, as reported by Mathew

[14]. The elevated maximum torque M_H and the reduced minimum torque M_L were observed as the amount of MAA and ZnO increased. At the beginning of the curing process, the liquid MAA mixed in the gum can temporarily act as a plasticizer in order to reduce the minimum torque M_L .

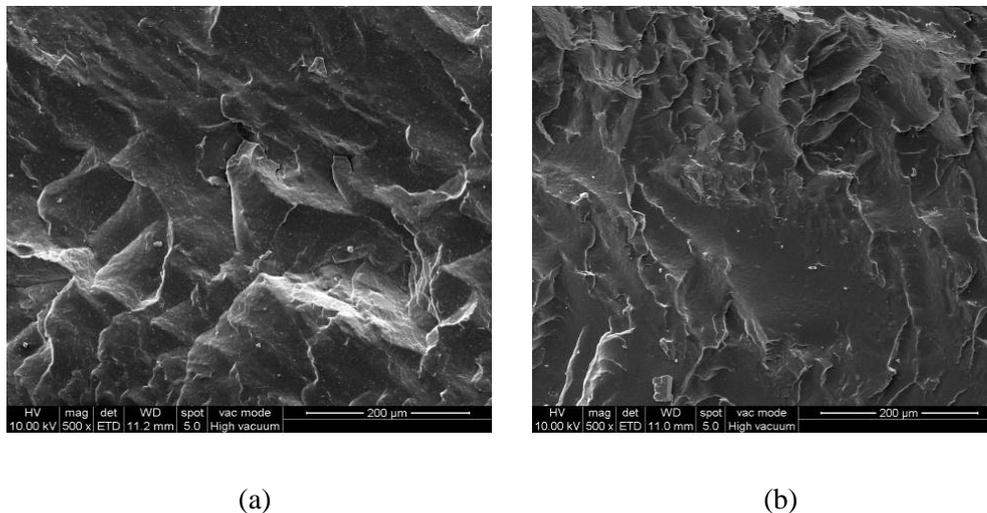


Figure 1. SEM photomicrograph of SBR/WRP blends, (a) unmodified SBR/WRP and (b) modified SBR/WRP.

Subsequently, the in-situ generation of ZDMA and the grafting of MAA to the rubber matrix triggered by dicumyl peroxide at the curing temperature lead to an increase in the maximum torque M_H .

The tensile strength of a 10 phr loading of unmodified WRP in an SBR matrix was reduced by approximately 15% as a result of the weak interaction between WRP and the rubber matrix. This resulted in the concentration of stress on the interface between the WRP and the rubber, causing failure of the material.

The mechanical properties gradually increased to a maximum at 16 phr of MAA, after which the further increase of MAA resulted in decreasing mechanical properties. As compared to the unmodified compound, the tensile strength and impact strength of the modified compound increased by 30% and 40%, respectively, while the modulus increased by 300% with an optimum loading of 16 phr MAA. This can be accounted for by the uniform dispersion of MAA and ZnO in rubber compounds below 16 phr of MAA loading, which contributes to the homogeneous dispensability of ZDMA and the grafting degree of MAA to the rubber matrix as reinforcement.

The total crosslinking density, ionic bond crosslinking density and covalent bond crosslinking density of the vulcanized rubber were all improved after modification. This is because MAA and ZnO reacted to generate an unsaturated carboxylic acid salt containing ionic bonds, and the composite network between WRP and the rubber matrix was created by the homopolymerisation of liquid MAA in swelled rubber powder and the rubber matrix with ZnO [15]. Additionally, the increased covalent bond crosslinking density was related to the double bond in the unsaturated MAA, which partially initiated the grafting on the rubber chain.

However, when more than 16 phr MAA was applied, the agglomeration of ZDMA became primarily responsible for the weaker interaction and bonding between the rubber substrate and the WRP, resulting in the deterioration of strength.

3.3. Dynamic compression fatigue of SBR/WRP composites

During the dynamic compression process, the generation of high dynamic compression was caused by the weak interface between the rubber powder and the rubber substrate. The addition of MAA/ZnO

enhanced the interface between the rubber powder and the rubber matrix by the in situ reaction, thus reducing the temperature increase induced by dynamic compression fatigue of the SBR/WRP composites. As shown in table 2, the increasing fatigue temperature of SBR with 10 phr unmodified WRP was 40.80 °C, and was significantly decreased after modification by the addition of the MAA/ZnO system. When the amount of MAA reached 16 phr, the fatigue temperature increased reached a minimum value of 30.25 °C, with a decreasing rate of 25%. The demonstrated variation tendency of the dynamic compression fatigue properties was consistent with that of the mechanical properties.

Table 2. Vulcanization characteristics, mechanical properties, crosslink density and compression fatigue properties of SBR/WRP/MAA compounds.

Sample	SBR	SBR/WRP 10					
		MAA 0	MAA 4	MAA 8	MAA 12	MAA 16	MAA 20
Cure Characteristic							
T _{S1} /min	0.85	0.93	0.65	0.53	0.48	0.50	0.48
T ₉₀ /min	22.02	20.58	19.50	20.20	18.58	17.83	16.37
M _I /dN m	5.4	4.04	2.44	2.03	1.99	1.87	1.66
M _H /dN m	20.12	19.57	23.62	33.19	38.27	44.98	40.36
Mechanical Properties							
Hardness (shoreA)/ °	65	64	67	74	76	78	78
300% Modulus/MPa	8.21	7.98	11.26	17.76	19.48	23.70	21.42
Tensile Strength/MPa	24.75	20.88	23.37	24.66	26.06	27.42	25.02
Elongation at Break /%	591	535	532	410	403	406	391
Permanent Deformation /%	10	8	10	12	16	16	16
Tear Strength/KN m ⁻¹	37.66	37.96	50.29	51.98	52.31	53.94	51.30
Crosslink Density/10⁻⁵mol ml⁻¹							
Covalent Crosslink Density	8.92	7.67	5.74	7.36	7.76	8.33	7.27
Ionic Crosslink Density	1.13	1.29	4.41	3.90	3.65	3.09	4.10
Total Crosslink Density	10.05	8.96	10.15	11.26	11.41	11.42	11.37
Fatigue heat buildup/°C	37.05	40.80	38.40	35.40	33.27	30.25	40.50

3.4. Dynamic mechanical property of SBR/WRP composites

The dynamic mechanical properties of SBR/WRP composites with and without MAA/ZnO modification were investigated. The tan δ versus temperature curves as shown in figure 2 depict the presence of sole tan δ matching with the glass transition temperature of the modified and unmodified SBR/WRP composites. For MAA/ZnO modified SBR/WRP, the storage modulus greatly increased, which can be attributed to the improved crosslinking density and corresponds to the higher hardness. The glass transition temperature (T_g) of SBR/WRP at -35.58 °C was near that of the modified SBR/WRP composite, which occurred at -37.40 °C. However, due to the restriction of the rubber chain movement induced by the improved crosslink density and the increased interaction between the rubber molecular chains and WRP particles, the value of the damping peak decreased in the MAA/ZnO modified SBR/WRP composite.

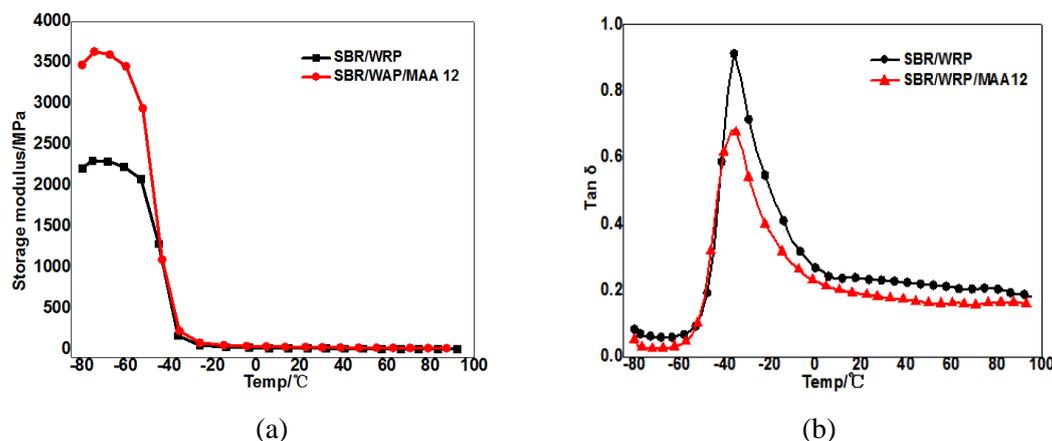


Figure 2. Dynamic mechanical property of SBR/WRP composites, (a) storage modulus and (b) loss tangent with temperature.

4. Conclusion

MAA/ZnO was employed to effectively modify SBR/WRP composites. The in situ generation of zinc dimethacrylate (ZDMA) and the grafting of MAA to the rubber chains improved the interfacial bonding of WRP and the SBR matrix. The total crosslinking density, ionic bond crosslinking density and covalent cross-linking density of vulcanizate were all increased, resulting in enhanced static mechanical performance and in the reduction of heat generated by dynamic compression. The glass transition temperature remained relatively unaltered, while the value of the damping peak decreased in MAA/ZnO modified SBR/WRP composites.

References

- [1] Formela K and Haponiuk J T 2014 Curing characteristics, mechanical properties and morphology of butyl rubber filled with ground tire rubber (GTR) *Iran. Polym. J.* **23** 185-194
- [2] Yu R, Gong Z, Guo W, Zhang H, Liu C 2016 A novel grafting - modified waste rubber powder as filler in natural rubber vulcanizates *J. Appl. Polym. Sci.* **133**
- [3] Zhu J, Zhang X, Liang M and Lu C 2011 Enhancement of processability and foamability of ground tire rubber powder and LDPE blends through solid state shear milling *J. Polym. Res.* **18** 533-539
- [4] Marković G, Veljković O, Marinović-Cincović M, Jovanović V, Samaržija-Jovanović S and Budinski-Simendić J 2013 Composites based on waste rubber powder and rubber blends: BR/CSM *Composites Part B: Engineering* **45** 178-184
- [5] Liu J, Liu P, Zhang X, Lu P, Zhang X and Zhang M 2016 Fabrication of magnetic rubber composites by recycling waste rubber powders via a microwave-assisted in situ surface modification and semi-devulcanization process *Chemical Engineering Journal* **295** 73-79
- [6] Lin Y, Chen Y, Zhang Y, Jia D, Luo Y and Liu L 2015 The use of zinc dimethacrylate functionalized graphene as a reinforcement in rubber composites *Polym. Adv. Technol.* **26** 423-431
- [7] Nie Y, Huang G, Qu L, Zhang P, Weng G and Wu J 2010 Cure kinetics and morphology of natural rubber reinforced by the in situ polymerization of zinc dimethacrylate *J. Appl. Polym. Sci.* **115** 99-106
- [8] Guo B C, Chen F, Chen W W, Lei Y D and Jia D M 2010 Reinforcement of nitrile rubber by in situ formed zinc disorbate *Express. Polym. Lett.* **4** 529-538
- [9] Yuan X, Peng Z and Zhang Y 2000 In situ preparation of zinc salts of unsaturated carboxylic acids to reinforce NB *J. Appl. Polym. Sci.* **77** 2740-2748
- [10] Wen S, Zhou Y, Yao L, Zhang L, Chan T W, Liang Y and Liu L 2013 In situ self-

- polymerization of unsaturated metal methacrylate and its dispersion mechanism in rubber-based composites *Thermochimica Acta* **571** 15-20
- [11] Huang A, Wang X and Jia D 2012 Preparation of HNBR/PMgMA/OMT nanocomposites and their aging resistance in different media *Acta Polymerica Sinica* **12** 660-665
- [12] Valentín J L, Carretero-González J, Mora-Barrantes I, Chassé W and Saalwächter K 2008 Uncertainties in the determination of cross-link density by equilibrium swelling experiments in natural rubber *Macromolecules* **41** 4717-4729
- [13] Nie Y, Huang G, Liu Z, Qu L, Zhang P, Weng G and Wu J 2010 Improved mechanical properties and special reinforcement mechanism of natural rubber reinforced by in situ polymerization of zinc dimethacrylate *J. Appl. Polym. Sci.* **116** 920-928
- [14] Mathew G, Singh R P, Lakshminarayanan R and Thomas S 1996 Use of natural rubber prophylactics waste as a potential filler in styrene-butadiene rubber compounds *J. Appl. Polym. Sci.* **61** 2035-2050
- [15] Xu C, Chen Y, Cao L, Wang Y and Zeng X 2013 Study of the Crosslinking Evolution of Styrene-Butadiene Rubber/Zinc Dimethacrylate Based on Dissolution/Swelling Experiments *Journal of Macromolecular Science, Part B* **52** 319-333