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Material properties

## Preparation, structure and properties of dynamically vulcanized polypropylene/acrylonitrile butadiene rubber/zinc dimethacrylate ternary blend composites containing maleic anhydride grafted polypropylene



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### ABSTRACT

This work demonstrated an approach to compatibilization between polypropylene (PP) and acrylonitrile butadiene rubber (NBR) by using maleic anhydride grafted polypropylene (MA-g-PP) as a compatibilizer in the presence of zinc dimethacrylate (ZDMA). It was observed that ZDMA increased the interfacial bonding between NBR and PP matrix. Incorporation of MA-g-PP further increased the mechanical properties of the resultant blends. The morphology analysis, dynamic mechanical analysis (DMA) and crystallization behavior study indicated that incorporation of MA-g-PP would change the polarity of the PP phase, facilitating more ZDMA diffusing from NBR into the PP phase during melt mixing. As a result, the possible creation resulted from polymerization of ZDMA combined with MA-g-PP increased the interface adhesion and compatibility between PP and NBR phases, which contributed to the considerable improvement in mechanical properties of the resultant blends. Moreover, we found that MA-g-PP did not influence the size of the crosslinked NBR phase, but significantly improved the viscosity of the resultant materials.

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### 1. Introduction

The simple blending of crystalline thermoplastic and elastomeric polymer results in a new class of material termed a thermoplastic olefin (TPO). The properties of the resultant TPO will be derived from the properties of each of the two polymers and dependent on the composition and

the interaction between their phases [1–4]. An approach to further improve the performance of TPO is to develop dynamically vulcanized TPO [5]. During dynamic vulcanization, the rubber is vulcanized in the presence of the molten thermoplastic under shear forces. Since crosslinked rubber is unable to coalesce, rubber particles are dispersed in the thermoplastic matrix even at high rubber content [5]. The effect of the dynamic vulcanization on morphology and mechanical properties has been extensively studied, and some important reviews are available in the scientific literature.

Acrylonitrile butadiene rubber (NBR) is a commonly used oil-resistant rubber. Polypropylene (PP)/NBR-based TPO combines the oil resistance of NBR as well as excellent

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chemical and moisture resistance, good ductility and stiffness, low density, and easy processing characteristics of PP [6]. The large difference in the solubility parameter between the polar NBR and the non-polar PP leads to poor compatibility of blends. As a result, PP and NBR are highly incompatible and usually exhibit phase-separated morphology because of poor physical, mechanical and chemical interactions across the phase boundaries [7]. The interfacial adhesion and mechanical properties of PP/NBR blends can be improved by the addition of compatibilizers or interfacial agents. Phenolic-modified PP and maleic anhydride-modified PP are two main types of compatibilizer for PP/NBR blends. George et al. [8–10] have reported several works about the effect of phenolic-modified PP and maleic-modified PP as compatibilizers on the properties of PP/NBR blends.

Zinc dimethacrylate (ZDMA) is highly reactive in the presence of free radicals and readily reacts with polymers. In recent years, it is found that rubbers can be reinforced by a high loading of ZDMA without conventional fillers such as carbon black and silica. ZDMA can be polymerized to graft onto rubber chains to enhance the crosslinked network of rubbers during peroxide vulcanization [11–14]. Considering the possible reactions of ZDMA, rubbers and PP in the peroxide free radical reaction, it is feasible to prepare PP/NBR/ZDMA ternary TPO via peroxide dynamic vulcanization, and hence to enhance the interfacial adhesion between PP and NBR with improved performance [15,16].

In the present work, we report a method for compatibilization of incompatible PP/NBR blends, using maleic anhydride grafted polypropylene (MA-g-PP) as a compatibilizer in the presence of ZDMA. Dynamically cured PP/NBR (80/20, w/w) blends loaded with ZDMA were successfully prepared via a two-step processing method. The effect of MA-g-PP on the processing, rheology, morphology, structure, crystallinity and mechanical property was evaluated by the mixing torque during dynamic vulcanization, rheometer, scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and mechanical properties measurement.

## 2. Experimental section

### 2.1. Materials

Polypropylene (PP, HP500N, MFI = 12 g/10 min (210 °C, 2.16 kg)) was purchased from CNOOC & Shell Petrochemicals Company Limited. Nitrile butadiene rubber (KNB 35LM) was purchased from Korea Kumho Petrochemical Co., Ltd (Korea). Zinc dimethacrylate (ZDMA) was purchased from Xian Organic Chemical Technology Plant (Shanxi, China). Dicumyl peroxide (DCP) was purchased from Sinopharm Chemical Reagent Co. Ltd (China) and was purified by anhydrous alcohol recrystallization before use. Maleic anhydride grafted polypropylene (MA-g-PP, AD105, MA content = 1.0 ~ 1.4 wt%) from Foshan Parkson New Material Co., Ltd. (Guangdong, China), was used as compatibilizer. The other chemicals were used as received.

**Table 1**

Formulations of the prepared samples (weight ratio).

Coding	PP	NBR	ZDMA	MA-g-PP	DCP
80/20-2-0	80	20	2	0	0.2
80/20-2-0.8	80	20	2	0.8	0.2
80/20-2-2.4	80	20	2	2.4	0.2
80/20-2-4	80	20	2	4	0.2
80/20-2-5.6	80	20	2	5.6	0.2
80/20-2-8	80	20	2	8	0.2

### 2.2. Compositions

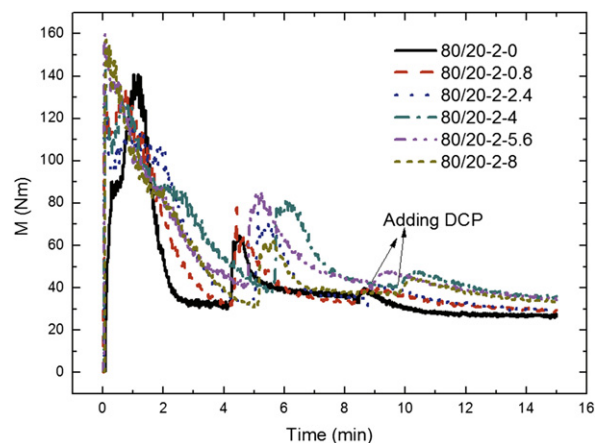
The compositions in terms of the weight ratios of components for PP/NBR/ZDMA/MA-g-PP blends are presented in Table 1. The PP-g-MA concentrations are varied from 1 to 10%wt of PP. For example, 80/20-2-2.4 denotes that the weight ratio of PP/NBR/ZDMA/MA-g-PP is 80/20/2.4, w/w/w/w.

### 2.3. Sample preparation

A two-step processing method was employed to prepare the dynamically vulcanized PP/NBR/ZDMA/MA-g-PP blends, in which the NBR and ZDMA were mixed to get rubber compounds, and then the rubber compounds were blended with PP and MA-g-PP melt.

The NBR/ZDMA compounds: Rubber compounds were prepared on a two-roll mill at room temperature.

Dynamically vulcanized PP/NBR/ZDMA/MA-g-PP blends: The blends were prepared in an internal mixer (Haake Rheocord 90) by melt mixing of the components at a temperature which was not more than 170 °C, and at a rotor speed of 50 rpm. In particular, the temperature of adding DCP was maintained at 165 °C, avoiding the rapid decomposition of DCP at a higher temperature (the half-life of DCP at 170 °C is approximately 1 minute). PP and MA-g-PP were first melted and then NBR/ZDMA compound was added. When the torque was stable, DCP was added and the mixing was continued until a final stable torque was reached. Subsequently, the blends were removed from the cavity of the internal mixer and cooled at room temperature before being



**Fig. 1.** Torques of PP/NBR/ZDMA/MA-g-PP composites during dynamic vulcanization.

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