Use of Micron-size Tire Rubbers in Recycled Thermoplastic Polyolefins to Improve Elastomeric Properties

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***Abstract*— Thermoplastic elastomers (TPE) including thermoplastic polyolefins (TPO) and thermoplastic vulcanizates (TPV) are promising elastomeric materials for automotive applications such as headlight surrounds, bumper covers, door gaskets, etc. TPEs offer a combination of great thermoplastic processability and outstanding rubbery properties, however, the process of recycling scrap and post-consumer products and reprocessing them into useful products have always been challenging. In addition, tire rubbers have been one of the most problematic sources to recycle, due to their large volume and durability. Innovative and effective methods are critical to reuse the recycled tire rubbers in value-added products other than their traditional use for fuel values. In this study, micron-size rubber powders (MRPs) were fabricated from recycled truck tires in large volume, and used as fillers for the twin screw extruder (TSE) compounding of recycled TPOs. TPO was chosen as the base resin for compounding because of its excellent reprocessability, good compatibility with the micron-size tire rubbers, and reasonable low cost. A compatibilizer was studied to enhance the uniform incorporation of micro-size rubber powders into the base resins and improve the overall performance of the compounds in a cost-effective way. The chemical structure of the recycled TPOs was confirmed by FTIR, and the thermal stability and compositional analysis of the recycled tire rubbers were characterized by TGA. The physical and mechanical properties (hardness, MFI, tensile, Izod impact, etc.) were extensively tested to study the overall performance of the compounds for automotive and commodity applications.**

I. INTRODUCTION

Thermoplastic polyolefin (TPO) rubbers have been used for a wide range of applications since their emergence in 1970s. Because of their good rubbery performance and weathering resistance, excellent processability and reasonable cost, they have been rapidly accepted in the automotive industries for products like bumpers, panels, gaskets and many other parts. [1] Commercial TPO materials are usually blends of polypropylene and ethylene-propylene-diene-monomer (EPDM) rubbers melt mixed together at various ratios of each propylene and EPDM component and possibly crosslinked to desired properties while the mixing occurs. This melt process achieves a high degree of distribution and dispersion of the EPDM, and leaves the elastomeric domains embedded within the continuous polypropylene matrix. [2] Commonly, various plasticizers like mineral oils and other additives like anti-ozonants and ultraviolet stabilizers and absorbers are incorporated into the blends to further enhance the weathering and aging properties. Postindustrial and postconsumer TPO materials are usually available in large quantities because of their popularity in automotive industry but it’s very challenging to re-use them since the recycled TPO can be either contaminated with colorants or require further processing. This limits its use in value-added products of high quality.

Recycled tire rubbers are another source of sustainable raw materials. Tire-derived fuel is the traditional use of shredded tire rubber chips (typically 1 inch or larger), and is still the primary market of scrap tires as of today. [3] Ground tire rubber is an emerging market that requires further processing to reduce the size of the rubber to meet different application demands. Coarse ground rubber, also called “crumb rubber” (usually 1/2-1/8 inch) and fine ground rubber (usually smaller than 10 mesh) are used for playground mulch, sports field infill, asphalt, molded or extruded parts, *et al*. [4] The growth of large-scale scrap tire processing has been traditionally limited by the product market development. [5] The recent development in crumb rubber processing techniques and equipment has advanced greatly because of the higher demands to discover many new value-added applications, and this leads to the result of micron-size rubber powder (MRP). The micron-size rubber powder (typically <80 mesh (177 µm)), due to their size, can be dispersed into many different material systems and therefore used for many products. For example, the use of MRPs in thermoplastic compounding systems can provide elastomeric properties, and much better surface smoothness and mechanical strength than conventional crumb rubber. MRPs can also be used in rubber-modified asphalt applications and new tire applications, and have shown superior performance and significant improvement in those cases. [6] An emerging area of interest in research and development of MRPs is the MRP/plastic compound, not only because MRPs can enhance elastomeric properties in the final products, but also provide a cost-effective solution to many applications, especially in automotive industries. From our perspective, continuous effects should be pushed on promoting the use of MRPs and adding more values in the extruded and injection-molded rubber/plastic parts.

In 2013, R. Ayyer and co-workers studied the effects of particle size of cryogenically-ground MRPs on the properties of MRP/polypropylene compounds. [7] However, to the best of our knowledge, little research has been done to investigate the interactions of MRPs with other plastic systems. In this study, MRPs were compounded in the TPO base resins using a twin screw extruder at various feed ratios. A polybutadiene-based compatibilizer was studied to enhance the bonding between MRP and TPO, and improve the overall performance of the MRP/TPO compounds. The chemical structure of the recycled TPO was confirmed by FTIR, and the compositional analysis of MRP and the TPO/MRP compounds was investigated by TGA. The physical and mechanical properties of the compounds were investigated to discover the potential automotive and commodity applications.

II. MATERIALS AND METHODS

A postconsumer TPO was used for this study. The TPO was recycled from automotive industries and reprocessed by McDonnough, Inc. The density and hardness of the TPO was 0.896 g/cm^3 and 92±2 (shore A), respectively. The micron-size rubber powders (MRPs) used in this study were ground and processed in ambient temperature from end-of-life truck tires, manufactured by Entech, Inc. The MRPs were metal-free and foreign matter-free. The size and size distribution of rubber particles were 60%-70% 80 mesh (177 µm) and 30%-40% 140 mesh (105 µm). A maleinized polybutadiene compatibilizer from Total Cray Valley (Ricon 131MA5, with Mn~4,700 g/mol) was experimented in an attempt to enhance the bonding and final properties of the TPO/MRP compounds.

Fourier transform infrared (FTIR) spectroscopy measurement was carried out to identify the recycled TPO materials on a Thermo Scientific Nicolet 4700 FTIR with a smart orbit Attenuated Total Reflectance (ATR) accessory. The TPO samples were vacuum dried and used for this purpose. The thermal stabilities and compositions of the MRP were analyzed by thermal gravimetric analysis (TGA). TGA was performed on TA Instrument (Discovery series) by heating the samples from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere, then switching the gas to air atmosphere and heating up to 850 °C at a heating rate of 10 °C/min.

The compounding of TPO and MRPs was performed by a co-rotating intermeshing twin screw extruder (Leistritz ZSE 40MAXX-40D, 41.4 mm). The TPO resin was fed through the main feeder and the MRPs were used as fillers in the side stuffer. Various ratios of TPO/MRP blends were extruded (90/10, 80/20, 70/30, 60/40, 50/50, 40/60). The extrudates were stranded and cooled in a water batch, pelletized, and dried thoroughly in a desiccant dryer at 50 °C. The extruder temperature profile is shown in **Table 1**.

The test specimens were injection molded by BOY 35E injection molding machine (39 ton) at 190 °C. The mold was cooled at 20 °C. The dimensions of the dumbbell tensile bars and the Izod impact strips were 16 cm × 1.2 cm × 0.3 cm and 6 cm × 1.2 cm × 0.3 cm, respectively. The tensile properties were tested by Zwick Roell Z010 TH AllroundLine with a non-contact lightXtens extensometer at a crosshead speed of 500mm/min according to ASTM standard D412. The Izod impact test was performed on a Zwick Roell basic pendulum impact tester with a manual notch cutter according to ASTM D256. The melt flow index (MFI) of the compound was measured by an extrusion plastometer (Zwick Roell BMF-002) according to ASTM D1238 (230°C, 10kg). The shore A hardness test (5 sec delay) was carried out on a Zwick Roell digital hardness tester (BH 04.3130). All tests were conducted at room temperature.

***Table 1**. Temperature profile in the extruder*

Zone	*Die*	*10*	*9*	*8*	*7*	*6*	*5*	*4*	*3*	*2*	*1*
T (℃)	180	180	180	180	190	200	210	220	220	220	220

III. RESULTS

The postconsumer TPO was characterized by FTIR to identify and confirm the chemical structure of the TPO used in this study. One challenge to use recycled materials is the contaminations and the mixed sources of different materials in the feedstocks. Our TPO feedstock was constantly checked for quality control to ensure the consistency in purity and property. **Figure 1** illustrates the FITR spectra of the postconsumer TPO and ethylene-propylene rubber (EPR), a key component of TPO. The peaks at 2917 and 2849 cm^{-1} are attributed to the C-H stretch, and the peaks at 1466 and 1376 cm^{-1} are attributed to the C-H bend, and the peak at 729 cm^{-1} are attributed to the C-H rocking vibrations. In comparison to the EPR spectrum, there is also a peak at 1727 cm^{-1} which corresponds to C=O vibrations in the recycled TPO spectrum. This indicates the ethylene vinyl acetate (EVA) residues which are commonly used as hot melt adhesives may exist in the postconsumer TPO.

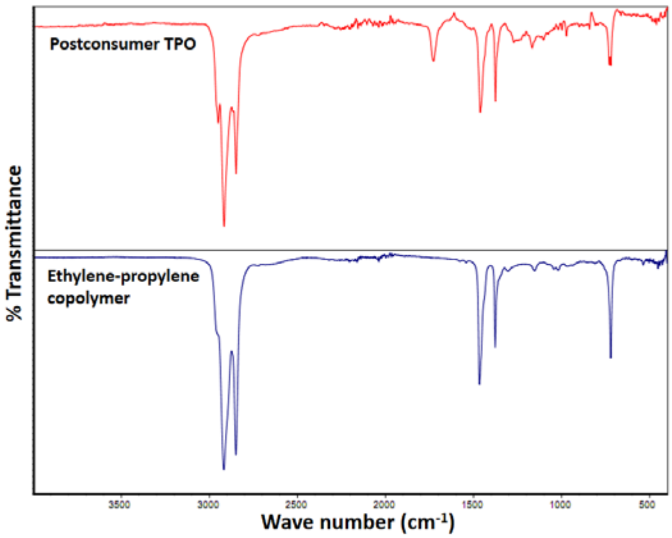

Fig. 1 *FTIR-ATR spectra of the reprocessed postconsumer TPO and the ethylene-propylene rubber (EPR). This confirmed the chemical structure "fingerprint" of the recycled TPO.*

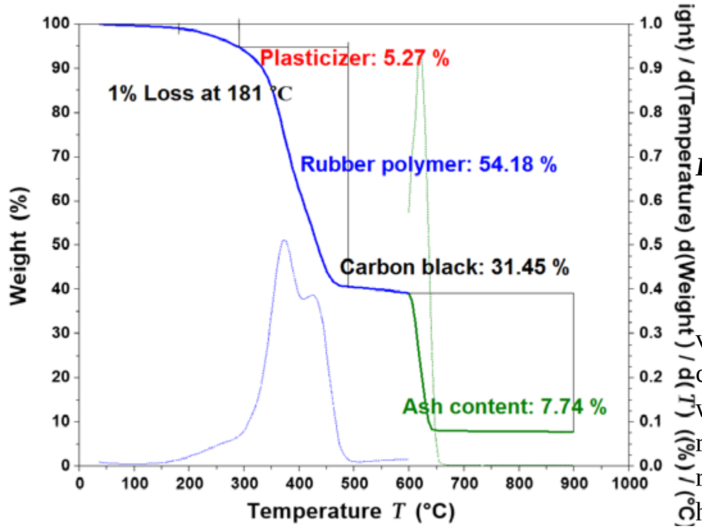

Fig. 2 *The TGA curve of the micron-size rubber powder (MRP). 1% weight loss at 181 °C. The compositional analysis was also performed, as shown in the graph.*

The thermal stability of the MRP (177 µm) used in this study was investigated by TGA, as shown in **Figure 2**. It was observed that the MRP remained thermally stable until ~180 °C. The 1% onset weight loss occurred at 181 °C. This result was used as reference to set the extruder zone temperature profile (**Table 1**). The reverse temperature profile was utilized deliberately to melt the TPO efficiently from zone 1-4 at 220 °C, and to prevent the high-degree decomposition of the rubber from zone 5-10, where the mixing performance of the extruder was optimal. The compositional analysis of the MRP was also performed to quantify the components of the rubber, namely oil, polymer, carbon black, and inorganic fillers, etc. The blue curve indicates the sample was heated in the nitrogen atmosphere while the green curve indicates the sample was heated in the air atmosphere. The highly volatile substances that equate to oils, process aids, and plasticizers and the medium volatile substances that equate to polymers were 5.27% and 54.18%, respectively. The combustion of the carbon black occurred when the sample atmosphere was changed to air, and 31.45% of carbon black was calculated before the samples burned out to the remaining ash (talc, etc.), which was 7.74%.

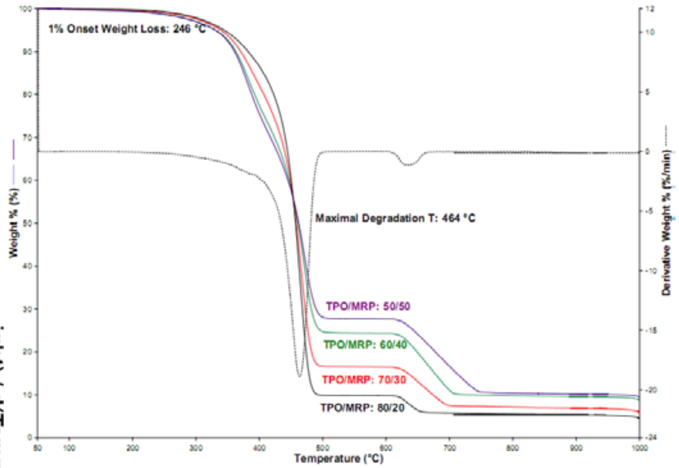

Fig. 3 *The TGA curves of the TPO/MRP compounds. 1% weight loss at 246 °C. Maximal degradation temperature at 464 °C.*

The thermal stability study on the TPO/MRP compounds at various ratios was shown in **Figure 3**. All the TPO/MRP compounds remained thermally stable until ~240 °C. The 1% weight loss at occurred at 246 °C, with maximal degradation rate at 464 °C. The residue percent was 5.3% and 10.1%, respectively for 80/20 and 50/50 TPO/MRP compounds, when heated up to 800 °C, indicating that higher loading ratios of MRPs, the higher ash content in the compounds.

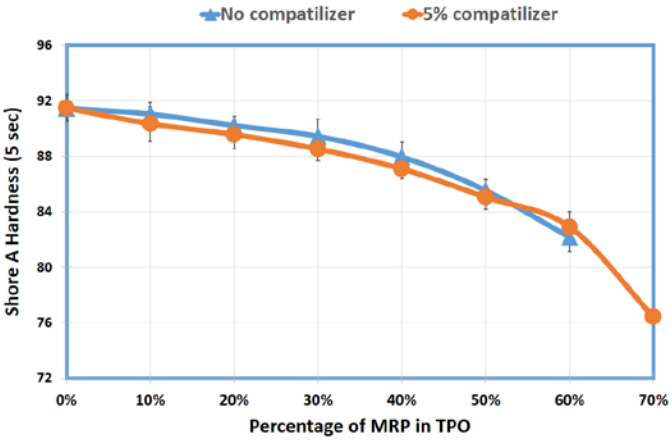

Fig. 4 *The Shore A hardness study on the TPO/MRP compounds of various rubber loading ratios, with 5% compatibilizer and without compatibilizer.*

The size of the rubber particles, the loading ratios of the rubbers in the base resin, and the compatibilizers are expected to influence the final properties of MRP/TPO compounds. The effect of the loading percentage of rubber with or without compatibilizers on the Share A hardness of the compounds is compared in **Figure 4**. As illustrated, the TPO exhibited a hardness of ~92 shore A. As the rubber loading ratio increased, the hardness started to slowly decrease in a relatively linear fashion from 92 to 85 shore A up to 50% rubber loading ratio. Once the percentage of the rubber exceeded 50%, the hardness decreased more dramatically. Therefore, the rubber loading ratios have a significant effect on the hardness of the TPO/MRP compounds, while the use of the compatibilizers did not have an effect. It is important to note that by using 5% compatibilizer, 70% of rubber in the TPO resin can be successfully achieved, while only 60% of rubber can be incorporated into the TPO without the compatibilizer.

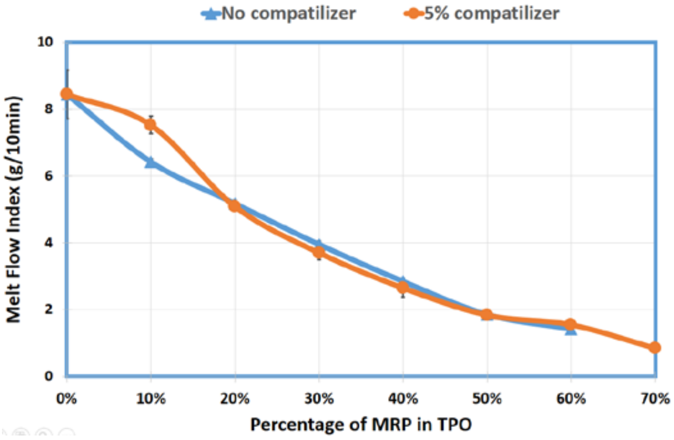

Fig. 5 *The Melt Flow Index (MFI) study on the TPO/MRP compounds of various rubber loading ratios, with 5% compatibilizer and without compatibilizer.*

The melt flow data on the TPO/MRP compounds of various rubber loading ratios is plotted in **Figure 5**. The MFI decreased with increasing the loading ratio of the rubber particles. This interpretates that the addition of the rubber particles in the TPO resin made the melt compound more resistant to flow. It is probably attributed to the crosslinked nature of the rubber networks when they're flowing as solids in the polymer melt, and also interfering the orientation and stretching of the TPO molecules in the flowing directions. The addition of the 5% compatibilizer in the TPO/MRP compound resulted in the same trend with a decrease in MFI. Also, the incoporation of the compatibilizer did not have an influence on the melt behaviors of the TPO/MRP compounds either.

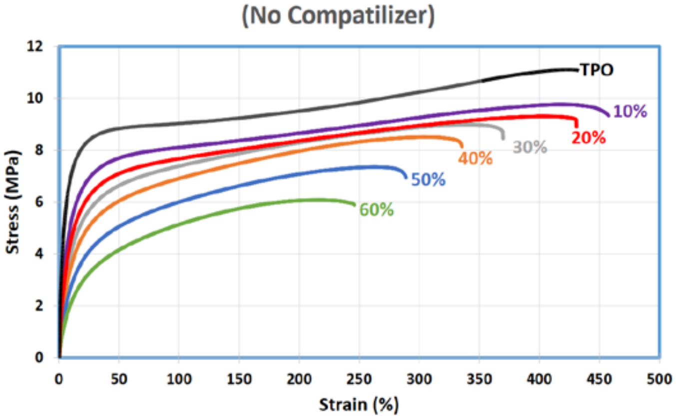

Fig. 6 *Comparison of the tensile stress-strain curves of the TPO/MRP compounds at various rubber loading ratios.*

The comparison of the tensile properties of the TPO/MRP compounds at various rubber loading ratios (frm 10% to 60%) was illustrated in **Figure 6**. As observed, the yield stress and the ultimate tensile strength (UTS) decreased as the rubber loading ratios increased. The Young's modulus and the elongation at break also dropped as higher percentage of rubber was added. It was also observed that the shape of the stress-strain curve transformed from a typical thermoplastic material (TPO) to a typical elastomer curve. It was speculated that the elastomeric properties of the rubber were incorporated into the thermplastic compound. In other words, the rubbery properties could be potentially enhanced while the excellent thermoplastic processibility is preserved.

Figure 7 shows the effect of 5% compatibilizer on the tensile properties of the TPO/MRP compounds at various rubber loading ratios. As expected, all the tensile properties included yield stress, UTS, elongation at break and Young's modulus decreased as the rubber loading ratios increased. The stress-strain curves with and without the compatibilizer are almost identical, implying that the addition of the compatibilizer had zero effect on the tensile properties.

The Izod impact test was conducted on the forward-notched samples, however, all the samples resulted in no break. This means the compounds were very tough and beyond the instrument testing capability, and the impact strength of all samples were higher than 580 J/m. However, it is expected that the impact strength should lower with the addition of rubber in the compound. This can also be observed in the stress-strain curves that the integrated areas below the curves decreased as rubber loading percentage increased.

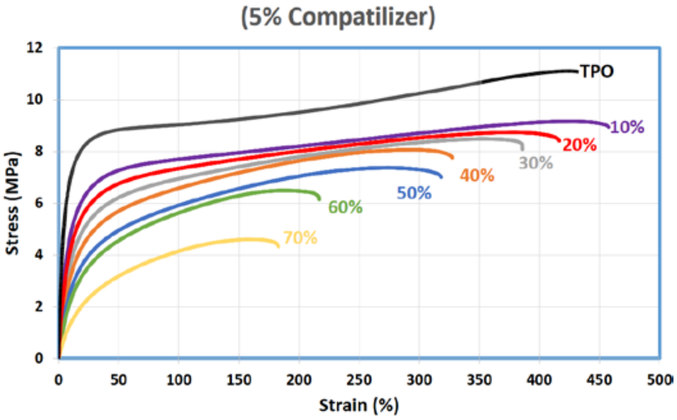

Fig. 7 *Comparison of the tensile stress-strain curves of the TPO/MRP compounds at various rubber loading ratios, with 5% compatibilizer.*

IV. CONCLUSIONS

The chemical structure of the postconsumer TPO was characterized and confirmed by FTIR. The thermal stability and the composition of MRP were analyzed by TGA. The MRP started to decompose at 181 °C. The compounding of MRP in TPO was successfully conducted at various rubber loading ratios. The addition and the loading percentage of the rubber had significant effects on the hardness, MFI and the tensile properties of TPO compounds. The hardness, MFI and the tensile properties decreased as the rubber loading ratios increased. For cost-effective applications, the balance between properties and the amount of rubber used in the TPO compounds should be weighed.

A maleinized polybutadiene compatibilizer was studied in this paper based on the chemical structures of the TPO and MRP. The addition of the compatibilizer did not have any influence on the physical and mechanical properties of the TPO compounds. This implies that the TPO has excellent compability with MRP, without the need of compatibilizers to enhance the bonding.

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