

## Investigation and Improvement of Thermal and Mechanical Properties of Recycled Polypropylene / Oxidized Polyethylene Composites

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### Abstract

In this study, different composites were prepared from oxidized polyolefin (OxPO) and synthetic waste (recycled polyolefin) to enhance the mechanical and thermal properties of recycled polyolefin, and the results of experimental studies on the mechanical (elongation, elasticity, tensile strength, etc.) and thermal properties of these composites were discussed. The composites were prepared in a laboratory-scale twin-screw extruder by grafting an oxidized polyolefin/styrene (St) blend onto recycled polypropylene (rPP) using the melt-free radical polymerization method. The prepared composites' mechanical properties (elongation and tensile strength) were determined according to the ISO 527-2 standard method. It was observed that the modulus of elasticity of (OxPO/St/rPP) composites increased by 24% compared to the modulus of elasticity of rPP and the tensile strength increased by 45% compared to the tensile strength of rPP. The composites were characterized by Thermogravimetric analysis and Fourier Transform Infrared (FTIR) spectroscopy. Thermogravimetric analysis (TGA) results showed that the thermal stability of the composites 36 °C increased compared to the thermal stability of rPP. Melt Flow Index (MFI) tests showed a 15% decrease in the Melt Flow Index value of the composites.

**Keywords:** recycled polypropylene; oxidized polyethylene; composite; styrene; maleic anhydride

### Geri Dönüştürülmüş Polipropilen / Oksitlenmiş Polietilen Kompozitlerin Termal ve Mekanik Özelliklerinin Araştırılması ve İyileştirilmesi

#### Öz

Bu çalışmada, geri dönüştürülmüş poliolefinlerin mekanik ve termal özelliklerini geliştirmek amacıyla oksitlenmiş poliolefin (OxPO) ve sentetik atıklardan (geri dönüştürülmüş poliolefin) farklı kompozitler hazırlanmış ve bu kompozitlerin mekanik (uzama, elastikiyet, çekme mukavemeti vb.) ve termal özellikleri üzerine yapılan deneysel çalışmaların sonuçları tartışıldı. Kompozitler, laboratuvar ölçekli çift vidalı ekstrüderde, oksitlenmiş poliolefin/stiren (St) karışımının geri dönüştürülmüş polipropilen (rPP) üzerine eriyik serbest radikal polimerizasyon yöntemi kullanılarak aşılansıyla hazırlandı. Hazırlanan kompozitlerin mekanik özellikleri (uzama ve çekme mukavemeti) ISO 527-2 standart yöntemine göre belirlendi. (OxPO/St/rPP) kompozitlerinin elastisite modülünün, rPP'nin elastisite modülüne kıyasla %24, kompozitlerin çekme mukavemetinin ise rPP'nin çekme mukavemetine kıyasla %45 oranında arttığı gözlemlendi. Kompozitler Fourier Transform Infrared (FTIR) spektroskopisi, Termogravimetrik analiz ile karakterize edildi. Termogravimetrik analiz (TGA) sonuçları, kompozitlerin termal stabilitesinin, rPP'nin termal stabilitesine kıyasla 36 °C arttığını gösterdi. Eriyik Akış İndeksi (MFI) testleri, kompozitlerin eriyik akış indeksi değerinde %15 düşüş olduğunu göstermiştir.

**Anahtar Kelimeler:** geri dönüştürülmüş polipropilen; oksitlenmiş polietilen; kompozit; stiren; maleik anhidrit

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## **1. Introduction**

Big bags are a versatile type of packaging that protects the products they contain from moisture, contamination, and UV light during transportation and storage. They are easy to fill and empty, offer high security, and can be tailored to the customer's exact requirements. Depending on requirements, big bags can be supplied with or without an inner liner, come with single or multiple carry handles, and are available in a range of sizes, colors, styles, and specifications. Big bags are industrial packaging with a load capacity of 500 kg to 2000 kg. The main elements of big bags consist of a main body, lifting handles, top and bottom closures, and filling and emptying spouts. These components are made exclusively from polyolefin (PO) raw materials. The cost of raw materials is the most important cost factor in the manufacture of these products. In Turkey, standard plastics (PE, PP, PVC, PS) account for the majority of plastic raw material consumption. The domestic supplier PETKIM covers around 35% of the demand for polypropylene (PP) and polyethylene (PE), thermoplastics derived from crude oil, which are mainly used for the production of large bags. Imports cover the rest of the demand. The current situation in the commodities market has led to fluctuations in oil prices and exchange rates. These external factors pose a threat to the competitiveness of the synthetic textiles sector, particularly due to lower labor costs in China and India, which have their oil resources. Recipe design and confidentiality, waste reduction, and improving raw material efficiency are key components to improving competitiveness. Thermoplastics increasing consumption, the fact that they are petroleum derivatives, the creation of uncontrollable waste mountains, and their environmental impact make the recycling of products made from polyolefins unsustainable. Disposal of plastic waste in the environment is considered to be a big problem due to its very low biodegradability and presence in large quantities [1,2]. Although recycling and reuse are sustainable methods to overcome these obstacles, the mechanical properties of polyolefins decrease during the recycling process.

Polyolefins are thermoplastic polymers with a wide range of applications, from automotive parts to textile and food packaging. Due to its low cost, thermal stability, and corrosion resistance [3-5], polypropylene is widely used for various applications such as packaging, technical automotive parts, and composites. Polypropylene which is produced by polymerizing the monomer propylene, is generally very resistant to chemical solvents. It is difficult for microorganisms in the environment to break down commercially produced plastics [6]. Despite numerous commercial applications, a major disadvantage of polyolefins (PP, PE) is their weak interaction with other materials. In addition, attempts to blend these types of polyolefins with other polymers have been unsuccessful for the reasons mentioned above. For example, if we want to overcome the incompatibility of polypropylene, we need to add polar groups to it. Like many other materials, PP forms only weakly interacting blends [7] because it lacks the chemical groups necessary for these interactions. It is a challenge to produce compatible blends or composites with PP without specific interactions [8]. The modification of polypropylene, i.e. the introduction of functional groups, makes it compatible with other materials. It has been found that PP modified with maleic anhydride significantly improves the impact strength and tensile strength of PP and LCP blends [9]. Many approaches, such as incorporating elastomers,

inorganic fillers, or blending with other polymers, can improve the thermal and mechanical properties of recycled PP [10-12].

Oxidized polypropylene is an oxidized polymer that contains peroxides and peracids in its structure in the presence of a strong oxidizing agent ( $H_2O_2$  or  $KMnO_4$ ) [13-15]. The presence of peracid-like groups in the polymer structure gives oxidized polypropylene certain properties (functionality, compatibility, solubility, etc.). It can therefore be used to create blends, compatibilized nanocomposites or to hold materials together. Due to their high strength and lightness, composite materials have a wide range of applications (defense industry, aerospace, automotive, transport, etc.) [16-18].

In this study, to improve the mechanical and thermal properties of recycled polypropylene, which are crucial for environmental waste reduction and sustainable production, composites were prepared by melt grafting into the polymer chain using monomers containing maleic anhydride (MAH) or styrene (St) with oxidized polyethylene (OxPE). To improve the overall performance of recycled PP, the methods developed by many researchers to produce long-chain branched PP were used and the branched structure was introduced into the recycled PP by reactive extrusion. The resulting composites were characterized and tested for their thermal properties. Test specimens were produced from dog bones and the composites were subjected to the ISO 527-2 standard test for fracture and elongation. The improvement in tensile strength of the composites compared to recycled polypropylene indicates the formation of a branched structure in the composites.

## **2. Material and Methods**

### **2.1 Materials**

Virgin polypropylene with MFI 4.3 g/10 min. (230 °C/2.16 kg) (PP, Sibur Sibex H043 FF/3). Oxidized polyethylene (OxPE, TRX K-90 Akdeniz Chemson). Benzoyl peroxide (BPO, 98% Merck). Maleic Anhydride (MAH, 99% BDH). Styrene (St, 99% Merck).

### **2.2 Calculations of the peroxide concentration of the oxidized polyolefin**

Calculations of the peroxide concentration of the oxidized polyolefin were determined by titration method. The following formula was used to calculate the acid number.

Definitions of the variables in the formula:

a: amount of thiosulfate consumed for the sample in the titration, ml

b: the amount of thiosulfate consumed for the blank in the titration, ml

N: normality of thiosulfate, N

m: amount of sample taken, g

$$\text{The acidity number} = \left\{ \frac{(a - b) \times N \times 1000}{m} \right\}$$

### 2.3 Preparation of synthetic waste

To simulate synthetic waste, virgin polypropylene with an MFI of 4.3 g/10 min (230 °C/2.16 kg) was thermally degraded at 260 °C with an L/D of 40 in a twin-screw extruder.

### 2.4 Preparation of mixtures

In reactive extrusion, depending on the solubility of the monomer in the polyolefin melt and monomer stability and volatility, the monomer can be added together with the polyolefin, added directly to the molten polyolefin, adsorbed onto another polymer or dissolved in a suitable solvent [19]. The recipes given as examples in Table 1 and Table 2 were prepared by mixing the monomer in oxidized polyethylene at a temperature of 70 °C for 15 minutes.

**Table 1.** Compositions prepared for blending with MAH and OxPE

Sample Name	OxPE (%)	MAH (%)
OX100	100	-
OX90MAH10	90	10
OX50MAH50	50	50
OX10MAH90	10	90
MAH100	-	100

**Table 2.** Compositions prepared for blending with St and OxPE

Sample Name	OxPE (%)	St (%)
OX50ST50	50	50

### 2.5 Preparation of the Composites

To prolong the polypropylene chains exposed to high temperatures and subjected to chain fragmentation by thermal degradation and/or to increase the molecular weight of the polymer, mixtures prepared according to the recipes given in Table 1 and Table 2 were added to the degraded polypropylene and passed through an extruder at 180 °C.

## **2.6 MFI Tests of the Composites**

The MFI tests of the prepared composites were performed on the Davenport MFI-10 apparatus according to ASTM 1238 B to monitor the changes in chain length and molecular weight of the prepared composites. The densities of the composites were measured using the AND GR-200 instrument. MFI and density measurements of composites are shown in Table 3 and Table 4.

## **2.7 Characterization of the composites**

The formation of functional groups on composites by thermal degradation was investigated using the PerkinElmer FTIR spectrometer. Figure 1 shows the FTIR analysis of the samples.

## **2.8 Tensile strength tests of composites**

To investigate the mechanical properties of composite OxPE/St/rPP, PP, and rPP samples in Table 4, dog bone-shaped specimens were prepared by injection molding and tested on WDW series universal testing machine (Hensgrand testing machine factory, China) by ISO 527-2 tensile test standard at  $(23 \pm 2)$  °C test atmosphere and  $(50 \pm 10)$  % relative humidity. Stress-strain curves are shown in Figure 2.

## **2.9 Thermal analysis of the composites**

Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) measurements were carried out using a Perkin-Elmer thermal analyzer. The mass of the samples was between 9 to 10 mg. The composite samples were heated in the range of 30-1000 °C with a flow heating rate of 10 °C/min under a nitrogen atmosphere. Thermal analysis thermograms are shown in Figure 2.

## **3. Results and Discussion**

An important disadvantage of polyolefins is their poor interaction with other materials. In this study, polypropylene, a polyolefin, was degraded through thermal degradation, and functional groups were created on its chains and mixed with other materials (such as monomers and other polymers, etc.) interaction has been increased. The acid number of the polymer was determined to find the number of functional groups formed during oxidation. for this purpose, an acid number of the oxidized polyethylene, which was used in this study to prepare composites for increasing the chain length of recycled polypropylene, was determined to be 40.80.

**Table 3.** Density and MFI values for rPP/OxPE/MAH composites, unmodified rPP, and virgin PP

<b>Sample Name</b>	<b>rPP (%)</b>	<b>OxPE (%)</b>	<b>MAH (%)</b>	<b>MFI (g/10min)</b>	<b>Density (g/cm<sup>3</sup>)</b>
1VPP	0	0	0	4.37	0.9024
2VPP	100	0	0	4.81	0.8846
2VPP <sub>Ox100</sub>	98	2.0	0	5.11	0,8940
2VPP <sub>Ox90MAH10</sub>	98	1.8	0.2	5.29	0,8995
2VPP <sub>Ox50MAH50</sub>	98	1.0	1.0	5.67	0,8910
2VPP <sub>Ox10MAH90</sub>	98	0.2	1.8	6.03	0,8876
2VPP <sub>MAH100</sub>	98	0	2.0	6.28	0,8890

The MFI values of the experiments prepared with styrene monomer decreased compared to the MFI values of rPP. The decrease in MFI value suggests that recycled PP, forming the composite matrix, intermingles with oxidized polyethylene and styrene monomer to elongate its chain.

**Table 4.** Density and MFI values for rPP/OxPE/St composites, unmodified rPP, and virgin PP

<b>Sample Name</b>	<b>rPP (%)</b>	<b>OxPE (%)</b>	<b>St (%)</b>	<b>MFI (g/10min)</b>	<b>Density (g/cm<sup>3</sup>)</b>
1VPP	0	0	0	4.45	0.9024
3VPP	0	0	0	5.98	0.8846
3VPP <sub>Ox50St50</sub>	99	0.5	0.5	5.10	0.8912

### 3.1 FTIR spectral analysis

The formation of functional groups by thermal degradation was studied using the FTIR method. Figure 1 shows the FTIR analysis of the samples. The carbonyl C=O peak around 1700 cm<sup>-1</sup> and the C-O ester peak around 1100 cm<sup>-1</sup> indicate the formation of functional groups. In addition, the overtone transitions observed around 2000 cm<sup>-1</sup> indicate the presence of a benzene ring structure.

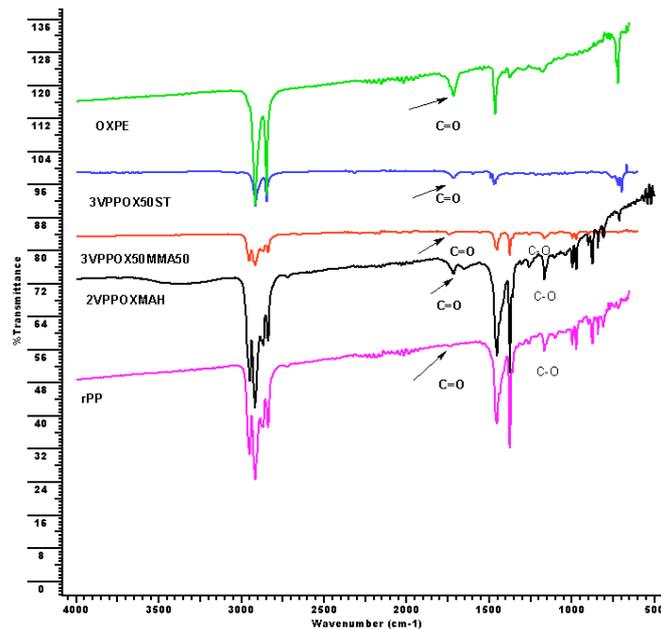


Figure 1. FTIR analysis of rPP/OxPE/St composites and rPP

### 3.2 Thermal analysis (TGA/DTG)

The TGA and DTG analyses are shown in Figure 2. It was found that all samples were degraded in a single step. The degradation temperature of PP, rPP, and composite starts at about 310°C and ends at 511°C. The degradation temperature ( $T_d$ , 5% mass loss temperature and  $T_d$ , 50% mass loss temperature) was also analyzed and it was found that the thermal stability of rPP was lower than that of the composites. It was found that the thermal stability of the composite of 1 wt% OxPE/St and rPP was about 36 °C higher than the thermal stability of rPP. When comparing the composite sample with the rPP sample, it was found that the temperature at which thermal degradation began ( $T_{onset}$ ) was 325°C and 343°C, respectively, and the temperature at which the samples were fully degraded ( $T_{offset}$ ) was 325°C and 343°C, respectively.

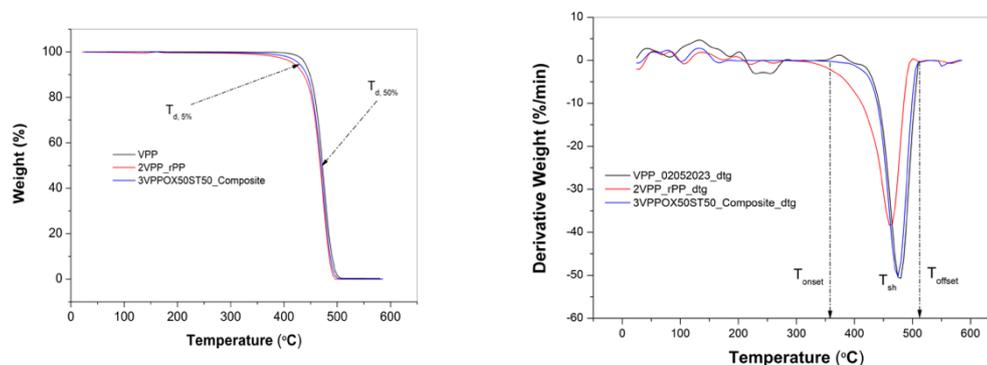


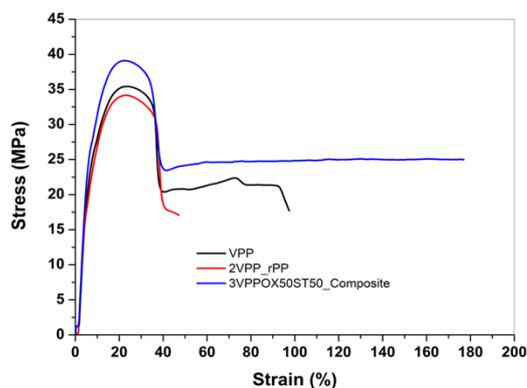
Figure 2. TGA and DTG analysis of rPP/OxPE/St composites, unmodified rPP, and virgin PP

**Table 5.** TGA results of rPP/OxPE/St composites, unmodified rPP, and virgin PP

Sample Code	rPP (%)	OxPE (%)	St (%)	Consent ( $\pm 0.5^\circ\text{C}$ )	T <sub>5</sub> ( $\pm 0.5^\circ\text{C}$ )	T <sub>50</sub> ( $\pm 0.5^\circ\text{C}$ )	T <sub>offset</sub> ( $\pm 0.5^\circ\text{C}$ )
1VPP	0	0	0	353	440	471	511
3VPP	100	0	0	310	418	467	492
3VPP <sub>Ox50St50</sub>	99	0.5	0.5	346	427	469	506

### 3.3 Mechanical properties of the composites

In the current study, the composites extracted from synthetic waste were treated with oxidized polyolefin (OxPO). Oxidized polyolefin/styrene (St) was grafted onto recycled polypropylene (rPP) by the radical polymerization method. Thus, a homogenous composite was obtained. The mechanical properties of the composites prepared with recycled PP and the recycled PP and virgin PP samples were tested with a tensile testing machine. In Table 3, a summary of the tensile tests for both PP and composites is presented. As a result, an increase in the tensile strength and elongation at the break of the composites prepared with recycled PP was observed. The stress-strain curves of PP, rPP, and the composites are shown in Figure 3.



**Figure 3.** Stress-strain graphs for PP, rPP, and the composites

**Table 6.** Mechanical properties of PP, rPP, and the composites

<b>Sample Code</b>	<b>rPP (%)</b>	<b>OxPE (%)</b>	<b>St (%)</b>	<b>Ultimate tensile strength (MPa)</b>	<b>Young's modulus (MPa)</b>	<b>Elongation (%)</b>
1VPP	0	0	0	36	1.1851	95
3VPP	100	0	0	34	0.8765	43
3VPP <sub>Ox50St50</sub>	99	0.5	0.5	39	1.0879	170

#### 4. Conclusion

In this study, to improve the mechanical and thermal properties of recycled polypropylene, composites of oxidized polyolefin (OxPO) and synthetic waste (recycled polyolefin) were produced and their mechanical (elongation, elasticity, tensile strength, etc.) and thermal properties were investigated. The test results show that the MFI values of the samples produced with styrene decreased or remained almost constant. The fact that the MFI values of the composite prepared with styrene and oxidized polyethylene and rPP remain constant may indicate an increase in molecular weight or the presence of cross-linking. The peak observed at 1730 cm<sup>-1</sup> in the FTIR spectrum indicates the formation of C=O and C-O - bonds leading to long chains. Experimental results on dog bone samples prepared with styrene formulations show a 45% increase in tensile strength and a 295% increase in elongation of recycled PP. A comparison of the modulus of elasticity of the composite and the rPP showed a 24% improvement in the modulus of elasticity of the composite.

#### Ethics in Publishing

There are no ethical issues regarding the publication of this study.

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