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Polypropylene HomoPolymer Oxidation in the Molten State Using Mixed Perovskite ($La_{0.9}Sr_{0.1}Ni_{(1-x)}Cr_xO_3$)

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Polypropylene HomoPolymer Oxidation in the Molten State Using Mixed Perovskite ($La_{0.9}Sr_{0.1}Ni_{(1-x)}Cr_xO_3$)

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To achieve oxidized polypropylene (OPP), polypropylene in molten state was reacted with mixed perovskite oxides ($La_{0.9}Sr_{0.1}Ni_{(1-x)}$ Cr_xO_3) using different concentration of oxidizing agent and varying reaction time. The modified polymer structure was then characterized using different experimental techniques such as Fourier transforming infrared (FTIR), Differential Scanning Calorimetry (DSC) and tensiometry and the melt flow index (MFI). FTIR results revealed that polar groups mainly carboxylic acids, ketones and esters have been performed in the OPP polymer structure while DSC analysis showed a decrease in the fusion temperature and an increase in glass transition temperature, compared to the original PP. In addition, solubility tests show that in contrast to the initial PP, OPP can be partially dissolved in polar solvents. Finally, it was concluded that by increasing the molar concentration of the oxidizing the agent and time of reaction, the number of polar groups increased.

Keywords: Oxidation, polar groups, perovskite oxides, molten polypropylene, oxidized polypropylene

1 Introduction

Polypropylene (PP) as an engineering material is widely used in the world especially during the last decades. Tertiary carbons, present in the isotac polypropylene polymer matrix, enhance its oxidation possibility (1–8) that affects the physical and mechanical properties of the produced complexes (9, 10).

The oxidation of PP leads to the formation of various end-products via initially formed hydro peroxides. Carbonyl groups, alcohols, C=C unsaturated bond, water and carbon oxides are examples of the products that can be found among volatile and nonvolatile products of the oxidized PP. These complexes can then be used as wax or compatibilizers in certain application.

The pioneering work reported by Libby and Pedersen made it possible to use perovskite complexes as oxidizing agents of hydrocarbons. On the other hand, many investigations have been done to explain the catalytic performance of these materials. It seems that these complexes act in such a way to make the release of oxygen species from the surface easier. The oxidation of paraffins, olefins, aromatics and oxygenate compounds are the most representative examples.

The combustion of methane over perovskite oxides has been extensively studied, particularly in recent years. The performance of these compounds for the combustion of other long hydrocarbon chains has also been examined. For example, Nakamura et al. and Nitadori and Misono studied propane combustion on Sr- or Ce-substituted $LaMO_3$ (M=Fe, Co) perovskites. The activity of $La_{1-x}Sr_xMnO_3$ varied in proportion to the reducibility of the catalyst surface, the amount of reversibly adsorbed oxygen, and the rate of isotopic equilibration of oxygen. Since all these properties are related to the surface oxygen, it can be concluded that the nonstoichiometric characteristic of the surface controls the catalytic activity. In another investigation, Kremenic et al. studied the combustion of polypropylene and isobutene at 573 K on $LaBO_3$ (B = Cr, Mn, Fe, Co, Ni) oxides and found the rates of isobutene combustion to be higher than those of propylene (24).

Carbonyl groups are detected by FTIR spectroscopy around 1720 cm^{-1}. It has been proved that the carboxylic acids play an important role in increasing the absorbance at this wave number region during photo and thermo oxidation (11, 12).

The loss of toughness in semi-crystalline polypropylene arises from oxidative chain scission in the amorphous region that involves one of the following conditions:

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Table 1. Oxidation conditions of Polypropylene in an internal mixer with a rotation speed of 60 rpm

Trial number	*PP (g)*	*Oxidation agent* $La_{0.9}Sr_{0.1}\ Ni_{(1-x)}\ Cr_xO_3$ *(mg)*	*Temperature (°C)*	*Reaction Time (min)*	*Other Conditions*	
Control sample	6	—	220(melt)	—	Pure only	N2
1	6	200	210	20	Pure only	N2
2	6	200	220	30	Pure only	N2
3	6	200	230	30	Pure only	N2
4	6	250	220	30	Pure only	N2
5	6	260	220	30	Pure only	N2
6	6	290	230	30	Pure only	N2

1. Tied molecule scission
2. Recrystallization of low molar mass polymer chains after scission
3. Increased polarity producing densification.

Oxidation of PP leads to the formation of oxygen-containing groups, which greatly affect the surface polarity of the polymer.

The evaluation of microstructure of oxidized PP using imaging methods such as UV microscopy in combination with 2, 4-dinitro phenyl hydrazine (DNPH) staining and chemiluminescence's imaging show that localized heterogeneities and regions of highly degraded polymer can coexist with the areas of practically nonoxidized material (13, 14).

In spite of the fact that oxidation of PP using different methods such as Co (II), Co (III) ions (15, 16), some peroxides and nitroxyl radicals (10), tetra butyl ammonium permanganate (TBAP), oxygen air and1-dodecanol as an accelerator (17–19), and $KClO_3/H_2SO_4$ (20) were studied and well documented, the oxidation of PP in the presence of perovskite oxides has received little attention. Perovskits has some advantages such as fewer polymers destroyed and less time needed for oxidizing PP. Therefore, we consider perovskits as an oxidizing agent for our research.

In this paper, the effects of perovskite as an oxidizing agent on melted PP were studied and the characteristics of the prepared oxide such as solubility in solvent, surface tension and thermal analysis were determined.

2.1 Materials

Polypropylene powder, without any additives with a grade of V 30 S, was obtained from Arak Petrochemical Co. (Iran). The melt flow index (MFI) was 16 g/10 min (190°C/2.16 Kg), and the isotacticity Index was 94–97%. The solvents MEK, toluene, THE, MeOH) and citric acid monohydrate were analytical grade and obtained from Merck Chemical Co.

2.2 Preparation of Perovskite Oxides

Perovskites ($La_{0.9}Sr_{0.1}Ni_{(1-x)}Cr_x\ O_3(0 \le x \le 1)$ (21)) were prepared by an amorphous citrate decomposition method. 10 ml of citric acid monohydrate solution (2 $mol.L^{-1}$) was added to 10 ml of a metal nitrates solution contained La $(NO_3)3\ 6H_2O$, Ni $(NO_3)2\ 6H_2O$, Cr $(NO_3)3\ 6H_2O$, $Sr(NO_3)2\ 6H_2O$. In order to form metallic amorphous citrates, this process should be done in such a way that the ratio of equivalent grams of the metals to equivalent grams of citric acid becomes one.

After evaporation of the solvent at 100°C, the obtained precursor was heated to 350°C for 2 h, and finally calcined in air at 800°C.

2.3 Preparation of Polypropylene Oxide

As seen in Table 1, a different amount of powdered $La_{0.9}\ Sr_{0.1}\ Ni_{\ (1-x)}\ Cr_xO_3$ was gradually added to molten PP under nitrogen atmosphere utilizing an internal mixer (a Brabender Plasti-Corder internal mixer PLE 331 of C.W. Brabender (South Hackenack, NJ)) with the rotational speed of 60 rpm.

2.4 Purification of Oxidized PP (OPP)

Oxidized PP was dissolved in toluene (at 80–85°C) and precipitated by pouring the solution into boiling methanol.

Table 2. Solubility of Oxidized PP (OPP) in warm MEK (70°C), THF (65°C) and cold toluene (25°C)

Polymer	*Oxidation Agent*	*Oxidation Temp. (°C)*	*Oxidation Reaction Time (min)*	*Solubility %*			M_n *(visco metric)*
				THF	*MEK*	*Toluene*	
PP	None	No oxidation	none	0	0	0	172400
OPP	Perovskite	210	20	8	10	8	141740
OPP	Perovskite	220	30	10	14	12	131100
OPP	Perovskite	230	30	13	15	13	112310

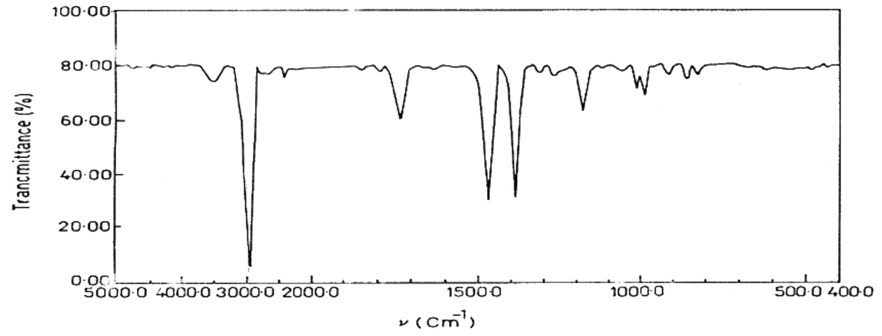

Fig. 1. FTIR spectrum of oxidized polypropylene (trial NO.2).

Separated particles were then washed with warm methanol (30°C) and dried under vacuum at room temperature. The recovered polymer was 89% of the original PP, about 7% of which was the oxidized PP, remained in the methanol-toluene solution indicating the high polarity of OPP.

2.5 IR Spectral Analysis

FTIR spectrum of OPP was studied using FTIR–4300 (Shimadzu Co). The spectral analysis was utilized to determine the effect of mixing time on producing esteric and ketonic groups in OPP and was carried out in the range 400–4000 cm^{-1}.

2.6 Thermal Analysis

Thermal properties of OPP were examined by DSC–700 Ulvac, SinkuRico Inc. The measurements were carried out with a heating rate of 20°C/min from room temperature to 220°C.

Thermal decomposition temperature measurement was carried out using a Thermogravimetric Analyzer V5.1A DuPont 2000, with a heating rate of 20°C/min from room temperature to 500°C.

2.7 Surface Tension

Surface activity of the polymer was investigated using automatic tensiometry (PROLABO). The melt flow index was determined using a MFI-592 motor Heizung.

Table 3. Absorption bands ratio between the carbonyl groups from ketones, esteric and methyl groups

Polymer	*Temperature (°C)*	*Mixing time (min)*	*Ratio between the Absorption Bands 1718–1741/1377*
OPP	230	10	0.0812
OPP	230	15	0.0918
OPP	230	20	0.1319
OPP	230	25	0.1615
OPP	230	30	0.1912

3 Results and Discussion

3.1 Solubility of Oxidized PP (OPP)

The solubility of the oxidized PP was studied and the results are given in Table 2. It can be inferred that variation in the polarity and type of oxidized groups lead to partial solubility of the oxidized PP in MEK and THF compared with PP, which is completely insoluble in MEK and THF.

In addition, it was shown that by increasing the temperature and time of the reaction, the solubility of OPP was increased due to arising polar groups in OPP; on the other hand, the molecular weight was decreased related to the breakage of the polymeric chains by enhancing the oxidizing treatment. It is notable that despite using lower temperature, the solubility power of toluene is similar to THF'S.

3.2 FTIR Analysis

Spectral analysis was performed on an oxidized sample prepared according to procedure mentioned for trial number 2 in Table 1 and the result is presented in Figure 1. Sharp absorption band can be distinguished at the 3518, 1741, 1718 and 1169 cm^{-1} region. The absorption band at 3518 cm^{-1} was attributed to the stretching mode of hydrogen bonded hydroxyl group in alcohols. The iodometric test indicated that there was no measurable amount of hydro peroxides in OPP.

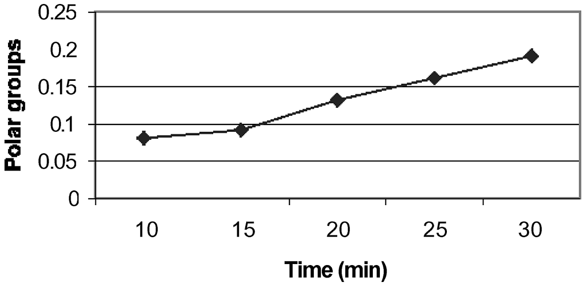

Fig. 2. Curve of the ratio between the absorption bands 1718–1741 cm^{-1}/1377 cm^{-1} vs. time oxidized at 230°C.

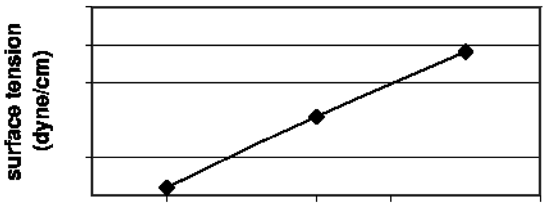

Fig. 3. Surface Tension vs. Temperature for the toluene contained OPP.

The stretching modes at 1741, 1718 and 1169 cm^{-1} were attributed to esteric, ketonic and C-O groups, respectively. The absorption bands ratios of polar groups and methyl was measured by FTIR as indicated in Table 3 and Figure 2.

It can be inferred that by increasing the mixing time, the ratio of 1718–1741 cm^{-1} band was raised that confirms the enhancement in producing esteric and ketonic groups in OPP.

3.3 Surface Tension

The surface tension measurement was performed on a sample solution prepared by adding OPP to toluene and the results are presented in Figure 3. The surface tension of toluene without any additives was 30.06 dyne/cm, while the results of the toluene contained OPP at 210, 220 and 230°C increased to 32.10, 33.05 and 33.91 dyne/cm, respectively, as shown in Figure 3.

It is notable that surface tension measurements addressed above are in accordance with FTIR results described previously.

The thermal stability of oxidized PP was assessed by thermogravimetric analysis (TGA). Thermal decomposition of an oxidized sample prepared according to procedure mentioned for trial number 3 in Table 1 was measured and compared with the results of the test performed on PP as shown in Figure 5.

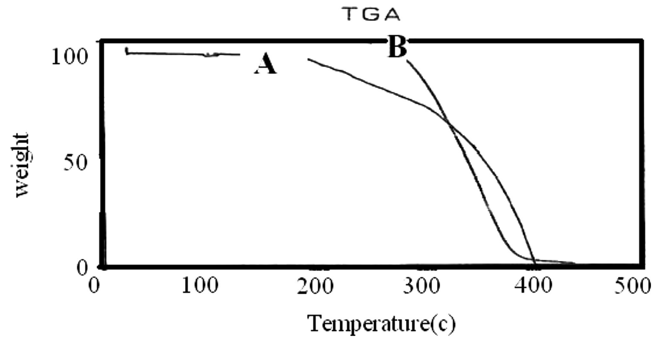

Fig. 5. TGA curves of (a) PP, (b) oxidized PP.

Onset of decomposition was lower (18.9%) than that's of PP due to the presence of thermo labile groups. Increasing the thermal stability of OPP may be attributed to the abstraction of labile hydrogen from the tertiary carbon atom, followed by generating graft chains (oxidation reaction) at the site.

On the other hand, it can be inferred that after decomposition of alcoholic, kenotic and esteric bonds in OPP, further thermolysis is probably similar to PP, however, OPP showed more thermal resistance in the temperature range of 305–400°C (Figure 5). This result probably arises due to a decrease on tertiary hydrogens in OPP.

The melt flow index was also measured and the results are given in Table 4. The results of the performed tests mentioned in Tables 2 and 4 show that by increasing the temperature, the amount of oxygen adsorption, MFI, surface tension and polarity of macromolecule chain increased. On the other hand, the molecular weights and fusion points decreased due to the formation of new chemical groups that facilitated the scission of covalent bonds and increased the structural variations.

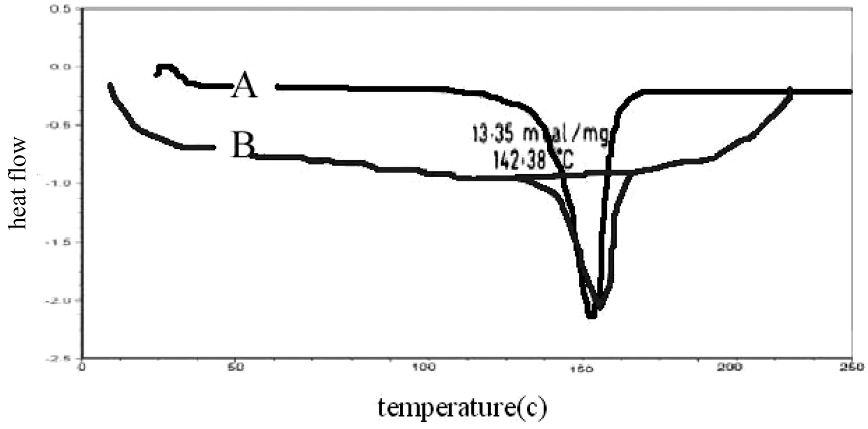

Fig. 4. DSC spectra of a) polypropylene, b) oxidized polypropylene.

Table 4. Melt Flow Index (MFI) and thermal analysis (DSC) results

Polymer	*Oxidation Agent*	*Oxidation Temp. (°C)*	*Oxidation Reaction time (min)*	*Fusion Temperature (°C)*	*MFI (190°C2.16Kg) (g/10 min)*
PP	None	No oxidation	None	168.15	16
OPP	Perovskite (200 mg)	210	30	158.38	20.8
OPP	Perovskite (200 mg)	220	30	152.5	22.5
	Perovskite (200 mg)	230	30	149.32	23.4

3.4 Proposed Reaction Mechanism

The result of FTIR indicated the presence of polar group such as ketones, alcohols and anhydrides. Some of the suggested mechanisms are given elsewhere (22, 23). It is known that perovskite generated free radicals. Thus, free oxygen radical's cases oxidation of PP.

4 Conclusions

In this study, the effects of perovskite as an oxidizing agent on melted PP were studied. The solubility, surface activity and thermal analysis of the prepared oxide found to be a function of both oxidizing agent concentration and reaction time.

As a summary, the following deduction can be obtained from the applied tests:

The amount of absorbed oxygen, surface tension, MFI and solubility in polar solvents and in toluene were increased by increasing the temperature and reaction time of oxidation. This observation can be related to enhancing the groups containing polar oxygen in OPP.

1. The oxidation reaction with Perovskite oxides mostly leads to the formation of esteric and keto-esteric groups, respectively.
2. The results of DSC indicate that polar groups present in oxidized polymer decreased the fusion temperature.
3. The oxidation reaction with Perovskite decreased the molecular weights and the crystallization of produced complexes.
4. Increasing the thermal stability of OPP may be attributed to the abstraction of labile hydrogen from the tertiary carbon atom, followed by generating graft chains (oxidation reaction) at the site.
5. After decomposition of alcoholic, kenotic and esteric bonds in OPP, further thermolysis is probably similar to PP , however OPP showed more thermal resistance in the temperature range of 305–400°C .

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