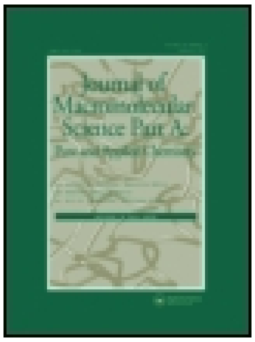

Journal of Macromolecular Science, Part A
Pure and Applied Chemistry

ISSN: 1060-1325 (Print) 1520-5738 (Online) Journal homepage: https://www.tandfonline.com/loi/lmsa20

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To cite this article: S. Assar, G. H. Zohuri, N. Ramezanian & S. Ahmadjo (2020): Synthesizing ethylene/1-octene copolymer and its nanocomposites with graphene and carbon nanotubes using a Ziegler−Natta catalyst, Journal of Macromolecular Science, Part A, DOI: 10.1080/10601325.2020.1774389

To link to this article: https://doi.org/10.1080/10601325.2020.1774389

JOURNAL OF MACROMOLECULAR SCIENCE, PART A: PURE AND APPLIED CHEMISTRY
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Synthesizing ethylene/1-octene copolymer and its nanocomposites with graphene and carbon nanotubes using a Ziegler – Natta catalyst

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ABSTRACT

Copolymerization of ethylene and 1-octene was carried out using a Ziegler-Natta catalyst and the optimization of copolymerization conditions was studied. The optimum polymerization activity was obtained at 60 °C and [Al]:[Ti] molar ratio of 143:1. It was observed that the increase in the comonomer ratio in the feedstock influenced the physical properties of the final copolymer obtained. The results showed a range of crystallinity (X_c) from 68.5% to 34.8% and a range of melting temperature (Tm) from 140 °C to 129 °C for the synthesized copolymers. The viscosity average molecular weight ($\bar{M}_v$) of the polymers decreased as the polymerization temperature increased, however, by increasing the monomer pressure, the $\bar{M}_v$ of the polymers and the catalyst activity increased. Polymer nanocomposites containing graphene and multi-walled carbon nanotubes with different particle sizes were prepared under the optimum copolymerization conditions. The addition of graphene and multi-walled carbon nanotubes decreased the activity of the catalyst. However, the thermal stability, and crystallinity of the polymers were found to be increased.

ARTICLE HISTORY
Received April 2020
Accepted May 2020

KEYWORDS
Ziegler–Natta catalyst; ethylene/1-octene copolymerization; nanocomposites; graphene; thermal stability

1. Introduction

Copolymers of ethylene with α-olefins are important products with favorable properties and are good alternatives to polyethylene. Furthermore, novel possibilities for controlling the properties of olefin copolymers have also recently become an important topic for researchers both in industry and in academia. Introduction of α-olefin comonomer into the polyethylene chain changes the structure and, consequently, the properties of the resultant polymer product. This change in structure depends on the type of catalyst system used, copolymerization conditions as well as the comonomer type that is introduced. It is known that longer comonomers such as 1-octene change the polyethylene properties, such as density, melting point and crystallinity more effectively than smaller units such as propylene at the same concentration.[1–6] In contrast to LDPE which is manufactured at high temperature and pressure, LLDPE and HDPE are conventionally synthesized via catalytic ethylene polymerization process at low temperature and pressure.[7] In particular, LLDPEs prepared using Ziegler – Natta catalysis have more uneven co-monomer distribution, whereas, a reverse trend is observed for those synthesized by metallocene catalysts.[1,4] Such difference in comonomer distribution is mainly attributed to the difference in the available active sites of catalysts that manifests itself in rheological and mechanical properties of the polymers as well as their melt miscibility. However, the density of polymer can be controlled by the ethylene/comonomer molar ratio, temperature, and catalyst type. The ability to crystallize a copolymer is affected by its molecular weight and concentration of branches and their distribution along the backbone of the copolymer.[1,4,8] In order to understand the crystallization behavior of branched molecules, more homogeneous fractions of a copolymer are required.[9] Among many polyethylene grades, the LLDPE offers many fascinating properties; however, its relatively low creep resistance, poor stiffness and electrical conductivity may limit its application in some fields. Nevertheless, the addition of a small amount of nanoparticles can improve the above mentioned weaknesses and result in polyethylene nanocomposites suitable for using in film, packaging and electronics industries.[1,7,10–12] The synthesis of nanocomposites can be performed by three techniques: solution, melt mixing and in situ polymerization.[11–15] Graphene and carbon nanotube have attracted the attention of researchers due to their outstanding reinforcing and modifying features. Ramazani et al., investigated in situ polymerization of polyethylene/clay nanocomposites using a novel clay-supported Ziegler-Natta catalyst.[12] Bahri et al., reported higher storage moduli of poly(1-hexene)/silica nanocomposites as compared to neat poly (1-hexene).[16] Alikhani et al., reported a HDPE/clay nanocomposite synthesized by a metallocene catalyst. A maximum degree of crystallinity of about 81% was obtained for HDPE/clay nanocomposites prepared by modified nanoclay.[17] Some metallocene-based polyolefin nanocomposites, reported by Kaminsky,[18] showed significant improvements

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in physical and chemical properties, such as stiffness, gas barrier, and flame retardancy. Furthermore, in the presence of graphene the catalyst activity decreased, because Ziegler-Natta catalysts are highly sensitive to polar additives and polar groups. Recently, some late transition metal catalysts have been demonstrated with great tolerance toward polar groups, therefore, some late transition metal catalysts may be great candidates for this purpose.[4,19] The M_w, thermal and electrical properties, storage and loss moduli of polymer improved in presence of graphene.[7,20] This study describes a detailed investigation of the effect of co catalyst, comonomer concentration, temperature and monomer pressure on the copolymerization of ethylene and 1-octene using a Ziegler-Natta catalyst. In addition, graphene and carbon nanotube were used in the synthesis of nanocomposites through in situ polymerization, and the thermal properties of resultant nanocomposites were investigated that less reported in literatures.

2. Experimental

All manipulations of air and/or water sensitive compounds were conducted under argon/nitrogen atmosphere using a glove box and/or standard Schlenk techniques. All the solvents were purified prior to use. Toluene (purity 99.9%) (Iran, Petrochemical Co.,) was dried over calcium hydride, refluxed over sodium/benzophenone, distilled under nitrogen and stored over activated 13X/4A° type molecular sieves for further drying before use. Ethylene (polymerization grade, purity 99.5%) and argon (purity 99.99%) were obtained from Maron Petrochemical Co. and Roham Gas Co., respectively, and were used after having been passed through activated silica gel, KOH, and column of activated 13X/4A° type molecular sieves. A Ziegler−Natta catalyst ($MgCl_2/TiCl_4$/TEA was obtained from Maron Petrochemical Co, Iran, with a Ti content of 2.8 wt%. Triethylaluminum (TEA) (purity 93%, Aldrich) was used as cocatalyst. 1-Octene (purity 97%, Merck) was stored over activated 13X/4A° molecular sieves and used without further purification. Multi-wall carbon nanotubes and graphene (purity 95%, Neutrino Co.,) were used as additional compounds for polymerization. For treatment of nanoparticles a mixture of the nanoparticle and triethylaluminum solution (TEA) was stirred (about 20 min prior to injection into the reactor) for mask the functional groups of nanoparticles (nanoparticles naturally contains functional groups such as water, carboxyls, hydroxyls, according to MSDS). In this state, TEA can act as an impurities scavenger. Low- and high-pressure polymerization processes were employed. The low-pressure process was carried out in a 100 mL round bottom flask equipped with a Schlenk system, vacuum line, ethylene inlet and magnetic stirrer. The high-pressure process (more than 2 bar) was carried out using a 1 L Buchi bmd − 300 (800 rpm) type reactor. The reactor was initially purged with nitrogen flow at 90 0C for 1 h, and then evacuated and purged with nitrogen several times, and then cooled to 40 °C. Toluene (35 mL), a desired amount of 1-octene, and TEA (1 M) were charged into the reactor under the pressure of ethylene monomer to remove impurities from the reaction system. The catalyst solution in toluene was charged and the ethylene pressure was increased to a desired pressure and the reactor was then heated up to a desired temperature. At the end of the polymerization reaction the acidified methanol (10%) was added. The suspension was stirred for 2 h and filtered, and the copolymer was dried at 60 °C under vacuum.

2.1. Characterization

The heat of fusion (ΔH_m) and melting temperature (T_m) were measured using differential scanning calorimetry (DSC) with a DSC Q100 Perkin Elmer. Polymer sample (10 mg) was weighed in a DSC pan, and DSC runs were performed at a heating rate of 10 °C/min in the range of temperature −100 to 250 °C, the melting temperature was measured at the first heating cycle. Morphology and shape of polymers were investigated by scanning electron microscopy (SEM VP 1450) operating at 7 and 15 kV, with aluminum stubs and gold metallization. Thermal properties were measured by a thermal gravimetric analyzer (Shimadzu-TGA 50, Perkin Elmer) from room temperature to about 1000 °C with a heating rate of 10 °C/min. Viscosity average molecular weight (M_v) of samples was determined according to the literature.[21] Intrinsic viscosity, $[\eta]$, was measured in decalin at 133 ± 1 °C using an Ubbelohde viscometer. Viscosity average molecular weight was calculated by the Mark-Houwink equation ($[\eta] = KM_v{}^a$, $\alpha = 0.69$, $K = 5.91 \times 10^{-4}$).[22,23]

3. Results and discussion

3.1. Effect of cocatalyst concentration

The main role of a cocatalyst in the polymerization process is to activate the catalyst (alkylation and creation of active sites in catalyst). It also acts as adsorbent of pollutants and chain transfer agent. As Table 1 show, by increasing the [Al]:[Ti] ratio to143:1, the catalyst activity increases, but the catalyst performance decreases with increasing the cocatalyst concentration. Initially, the catalyst activity increases to an optimal value due to the creation of active sites through alkylation (Table 1). Reducing the activity of the catalyst can be due to the excessive combination of TEA and active sites and, consequently, their inability to combine with monomers.[24] High concentration of cocatalyst leads to alter the structure of active sites by displacing chlorine groups with alkylic groups and, consequently, reduce the activity of catalyst.[25]

Table 1. Effect of cocatalyst concentration on polymerization.

Sample	[Al]:[Ti] (molar ratio)	Yield (g)	Activity gPE/(mol cat.h)$\times 10^{-5}$
A	71:1	1.7	0.6
B	107:1	3.0	1.1
C	143:1	3.9	1.4
D	214:1	3.0	1.1

Polymerization conditions: Toluene = 35 mL; ZN catalyst = 2.8×10^{-5} mol/l; 1-Octene: 2×10^{-2} mol/l; Ethylene gas pressure =1.5 bar; Temperature = 60 °C; Time = 1 h.

Table 2. Effect of comonomer concentration on polymerization.

Sample	Comonomer concentration in the feed (mol/l)	Yield (g)	Activity g PE/(mol cat.h)$\times10^{-5}$	T_m (°C)	ΔH_m (J/g)	X_c (%)
E	0	3.9	1.4	140	197.3	68.5
F	2.0×10^{-3}	3.7	1.3	135.1	196.1	68.1
B	2.0×10^{-2}	3.4	1.2	131.2	170	59
G	4.0×10^{-2}	2.3	0.82	130.7	134.2	46.6
H	6.0×10^{-2}	1.5	0.54	129.3	100.2	34.8

Polymerization conditions: Toluene = 35 mL; ZN catalyst = 2.8×10^{-5} mol/l; [Al]:[Ti] = 143:1 (molar ratio); Ethylene gas pressure = 1.5 bar; Temperature = 60 °C; Time = 1 h.

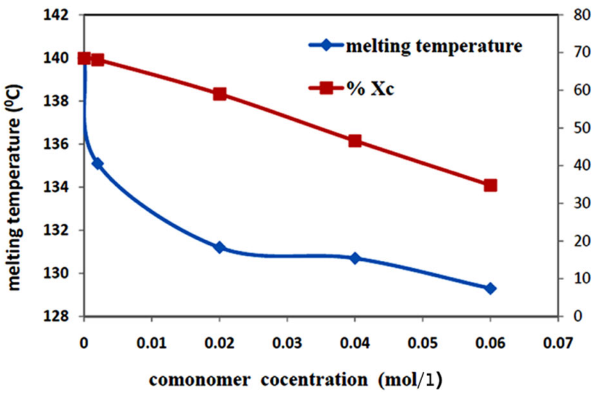

Figure 1. Effect of comonomer concentrations on melting temperatures and crystallinity contents.

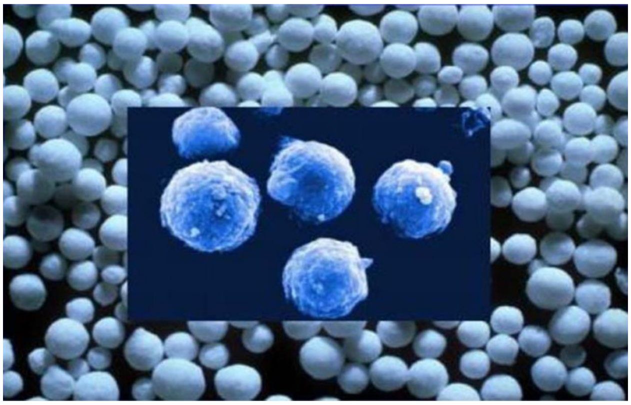

Figure 2. Electron microscope image of catalyst particles, magnification 1000×.

3.2. Effect of comonomer concentration on polymerization

In copolymerization of ethylene with α-olefins, the amount of catalyst activity is always affected by α-olefin, which is known as the effect of comonomer. This effect varies in several ways, such as polymerization conditions and catalyst type. In general, the different behaviors which are usually observed with the addition of a comonomer are due to the effect of a comonomer on active catalyst sites. Also, the introduction of a comonomer into a growing polymer chain affects the catalyst active sites and polymer dissolution. The presence of a comonomer in the polymer chain improves its dissolution properties, especially, at low temperatures and reduces monomer transfer resistance. The properties of a polyolefin copolymer are influenced by the amount of comonomer.[26] By increasing the amount of 1-octene in the feed, the catalyst activity decreased (Table 2).

A comonomer with a large size and large spatial hindrance prevents the incorporation of ethylene monomer and, as a result, reduces the catalyst activity.[27] It should also be considered that the reactive ratio of 1-octene comonomer is much lower than that of ethylene in the copolymerization.[28] By increasing the amount of comonomer in the input feed, the melting temperature and polymer crystallinity decreased due to increase in the number of short-chain branches present in the main chain (Table 2).[29–32]

The melting temperature of the polymers reduced from about 140 °C to 129 °C and their crystallinity decreased from 68% to 34% relative to the polyethylene homopolymer (Figure 1 and Table 2). The drop in melting temperature is very severe in a range of low concentrations of comonomer and decreases with a slight slope with increasing the concentration of the comonomer. The crystallinity percent of the samples changed linearly in the studied area (Figure 1).

The effect of comonomer on the polymer morphology was investigated using SEM images. Since the spherical shape of the polymer particles is the most attractive form due to many reasons, including the maximum possible movement of polymers during processing, the study of morphology is of great importance. Various factors affect the morphology of polymer powder. The most important factor is the morphology of catalyst particle. Based on the principle of replication, the shape of the polymer produced has a direct relation to the shape of the catalyst particle used in polymerization.[33] Other factors, such as polymerization conditions, also affect the morphology of the polymer.[34] Figure 2 shows the electron microscopic image of a number of catalyst particles, which are completely spherical and unique.[35] Two polymer samples E and F (Table 2) produced, respectively, from ethylene homopolymerization and ethylene and 1-octene copolymerization were selected. The shape of polyethylene produced from homopolymerization has large particles but mainly with irregular shape and a small number of spherical forms, but these spherical particles were less observed in the corresponding copolymer, which is probably due to the polymerization conditions and the presence of 1-octene comonomer (Figure 3).

3.3. Effect of polymerization temperature

The polymerization activity was increased with increasing polymerization temperature from 50 °C to 60 °C (Table 3), that maybe related on polymerization conditions, and reactor type that used, the industrial ZN catalysts are usually show optimum activity in temperatures near 80 °C. Increasing the polymerization temperature above the 60 °C reduced catalyst activity gradually, that can be due to deactivation of active catalytic sites (chemical agent) and the

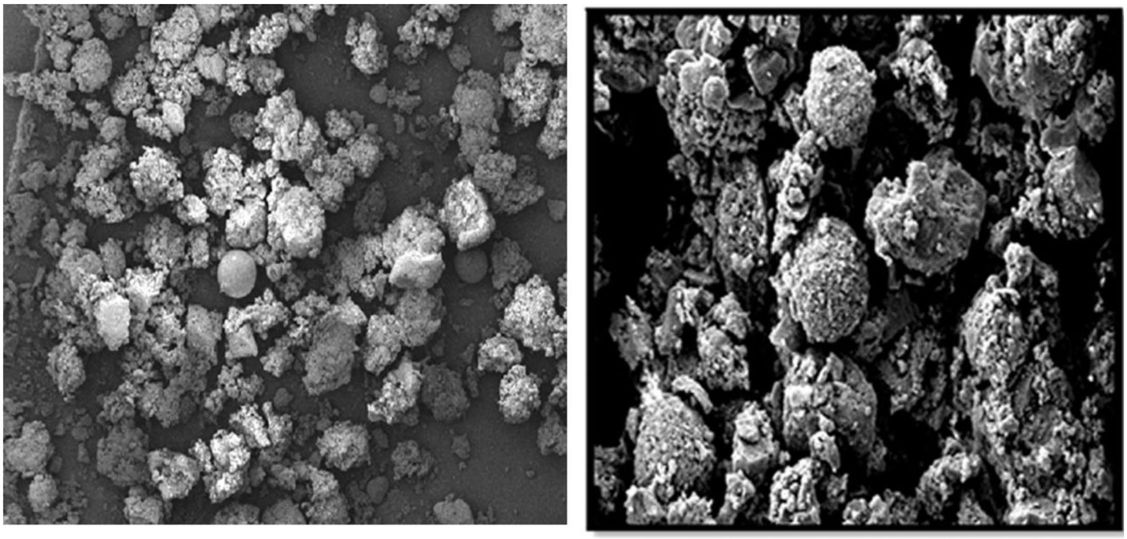

Figure 3. SEM images homopolymer samples E (left), (magnification of 500×) and copolymer F (right), magnification 1000×.

Table 3. Effect of temperature and monomer pressure on polymerization.

Sample	Temperature (°C)	Pressure (bar)	Yield (g)	Activity g PE/(mol cat.h)$\times 10^{-5}$	Mv (g/mol)
I	50	1.5	2.9	1.03	1.3 × 106
B	60	1.5	3.5	1.30	6.0 × 105
J	70	1.5	3.0	1.07	3.8 × 105
JJ	80	1.5	2.7	0.96	3.5 × 105
K	60	0.5	0.1	0.04	–
L	60	1.0	1.0	0.36	2.5 × 105
M	60	3.0	5.0	1.78	3.0 × 106

Polymerization conditions: Toluene = 35 mL; ZN catalyst = 2.8 × 10^{-5} mol/l; [Al]:[Ti] = 143:1 (molar ratio); 1-Octene: 2 × 10^{-2} mol/l; Time =1 h.

reduction of monomer solubility (an effective physical factor) in the reaction media.[36]

The viscosity average molecular weight (M_v) of polymer samples I, B, J and JJ (Table 3) obtained at 50, 60, 70 and 80 °C, are 1.3 × 106, 6.0 × 105, 3.8 × 105 and 3.5 × 105 g/mol, respectively. By increasing the polymerization temperature from 50 to 80 °C, the viscosity average molecular weight decreased (Table 3). The higher polymerization temperature facilitated the chain transfer reaction, which decreased the M_v of obtained polymers.[37]

3.4. Effect of monomer pressure

Copolymerization was carried out at various pressures of monomer (ethylene) from 0.5 to 3 bars (Table 3). Increasing ethylene pressure increases the concentration of ethylene in the reaction media. Monomer pressure has been considered as an important factor in the polymerization process of gaseous monomers. According to Equation (1), there is a direct relation between the polymerization rate and the monomer pressure; therefore, with increasing ethylene pressure, the amount of polymer obtained was also increased.[38,39]

$$R_p = k_p C^* [M]^n \tag{1}$$

where R_p is the propagation rate, k_p is the rate coefficient, C^* is the active sites concentration, M is the monomer concentration and n is order of polymerization reaction.

Table 4. Effect of polymerization time on catalyst activity.

Sample	Time (h)	Yield (g)	Activity g PE/(mol cat.h)$\times 10^{-5}$
N	0.5	1.5	1.1
B	1.0	3.5	1.2
O	1.5	4.3	1.0
P	2.5	5.5	0.8

Polymerization conditions: Toluene = 35 mL; ZN catalyst = 2.8 × 10^{-5} mol; [Al]:[Ti] = 143:1 (molar ratio); 1-Octene: 2 × 10^{-2} mol; Ethylene gas pressure = 1.5 bar; Temperature = 60 °C.

The viscosity average molecular weight (M_v) of polymer samples L, B, and M (Table 3) was increased by increasing the pressure from 1 to 3 bars. This ascending trend is due to increased monomer concentration, which is more likely to enter the polymer chains and to increase the molecular weight.[40,41]

3.5. Effect of polymerization time

Polymerization was carried out at different polymerization times from 30 min to 2.5 h (Table 4) .As the data showed, initially with increasing polymerization time, the catalyst activity is increased. This increase continued until about an hour, but after that, the catalyst activity declined until the time reached 2.5 h. By passing the time, there is also the possibility of thermal deactivation of active centers, which reduces the catalyst activity.[42]

Table 5. Effect of nano additives on polymerization.

Sample	Type and amount of additives (mg)	Yield (g PE)	Activity g PE/(mol Cat.h)$\times 10^{-5}$	T_m (°C)	ΔH_m (J/g)	X_c (%)
B	–	3.5	1.2	131.2	170.0	59.0
Q	Graphene: 10 mg	3.0	1.07	131.8	196.9	68.4
R	Graphene: 30 mg	2.8	1	132.1	197.2	69.1
S	CNT 20-30 nm: 10 mg	2.5	0.89	133.3	172.9	60.0
T	CNT 20-30 nm: 30 mg	2.2	0.78	134.1	175	61.2
U	CNT 30-50 nm: 10 mg	2.0	0.71	135.3	217.6	75.6
V	CNT 30-50 nm: 30 mg	1.7	0.6	136.2	219	76

Polymerization conditions: Toluene = 35 mL; ZN catalyst = 2.8×10^{-5} mol; [Al]:[Ti] = 143:1 (molar ratio); 1-Octene: 2×10^{-2} mol; Ethylene gas pressure = 1.5 bar; Temperature = 60 °C; Time = 1 h.

Table 6. Effect of nanoadditives on thermal resistance of polymer samples.

Sample	Type and amount of additives (g $\times 10^{-3}$)	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	$T_{d95\%}$ (°C)	Residue at 800 °C (CR)	LOI	Temperature (°C)	Time (s)	Degradation state
B	–	433.3	478.8	498.6	6.82	20.2	478.8	2723	Beginning of Degradation
							523.5	2989	Degradation
							769.3	4466	End of Degradation
Q	Graphene: 10 mg	442.6	484.6	503.3	12.2	22.4	489.3	2786	Beginning of Degradation
							520.8	2975	Degradation
							804.3	4676	End of Degradation
S	CNT 20–30 nm: 10 mg	438	483.5	503.3	20.54	25.7	488.2	2779	Beginning of Degradation
							520.8	2975	Degradation
							802	4662	End of Degradation
U	CNT 30–50 nm: 10 mg	446.1	485.8	505.6	13.47	22.9	490.5	2793	Beginning of Degradation
							523.2	2989	Degradation
							802	4662	End of Degradation

Polymerization conditions: Toluene =35 mL; ZN catalyst =2.8×10^{-5}mol; [Al]:[Ti] = 143:1 (molar ratio); 1-Octene: 2×10^{-2} mol; Ethylene gas pressure =1.5 bar; Temperature = 60 °C; Time =1 h.

3.6. Ethylene/1-octene polymerization using graphene and multi-walled carbon nanotubes

The combination of soft polyethylene matrix with hard nanoparticles greatly impacts and improves the properties of the resulting nanocomposite.[43–45] The absence of functional and polarity groups in the polyethylene chain leads to incompatibility between polyethylene and graphene or carbon nanotubes and other additives such as pigments, fillers, and so on. In ethylene polymerization with using Ziegler – Natta catalyst, graphene and carbon nanotubes can be simultaneously added to the reaction mixture, while polyethylene chains are growing on the polymer surface. However, strong covalent bonding or interactions between the polyethylene chains and these additives cannot be formed during polymerization.[46–50] The addition of graphene and carbon nanotubes reduces the activity of the catalyst, because these additives have functional groups that can directly poison catalytic active centers (Table 5). By adding graphene and carbon nanotubes, the melting temperature and crystallinity percent of polymer nanocomposites are increased compared to those of control sample (Table 5). The increase in melting temperature is probably due to a slight increase in thermal resistance of polymer specimens, the nanocomposites were more crystalline. An increase in the percentage of crystallinity in polymer nanocomposites may also be due to the nucleation effect of nanoparticles.[43,44] By increasing the amount of different nanoparticles in the polymerization, the melting temperature and crystallinity of obtained nanocomposites slightly increased (samples T and V). The greatest increase in these parameters is related to carbon nanotubes with the size of 30–50 nm.

Thermal properties of the control sample and polymer nanocomposites were investigated using TGA analysis. The limited oxygen index (LOI) parameter is used to determine the oxidation resistance value. LOI is the oxygen content required to oxidize a small amount of sample in a container. Char yield (CR) is used to determine the limited oxygen index. The amount of char remaining at 800 °C depends on the substance and the amount of additive. The LOI was calculated from the Krevelen-Hoftyzer equation (Equation (2)).[50] The results showed that the samples containing graphene and carbon nanotubes had higher oxidation resistance than the control sample (Table 6).

$$\mathrm{LOI} = 17.5 + 0.4\mathrm{CR} \tag{2}$$

According to Table 6, the initial degradation temperatures of the control sample and samples Q, S, and U are 478.8 °C, 489.3 °C, 488.2 °C and 490.5 °C, respectively, which show that the thermal resistance of the samples containing additives is increased. The $T_{d5\%}$ (degradation temperature of 5% weight loss) of the control sample was 433.3 °C, but that of the Q sample having graphene additive was 442.6 °C (i.e., 9.3 °C higher than the $T_{d5\%}$ of the control sample), samples S and U showed similar behaviors. This increase is due to the high thermal resistance of nanoparticles and their physical interactions with the polymer chains. These interactions prevent the movement of polymer chains and lead to increase the thermal resistance of nanocomposite. In 50% degradation of the sample containing graphene, there was 5.8 °C temperature increases relative to the control sample. For the 95% degradation, the temperature increased 4.7 °C. The $T_{d50\%}$ and $T_{d95\%}$ for samples S and U were higher than sample B.

3.7. Morphological study of polymers

Scanning electron microscope images of polymer samples were investigated in the presence and absence of additives

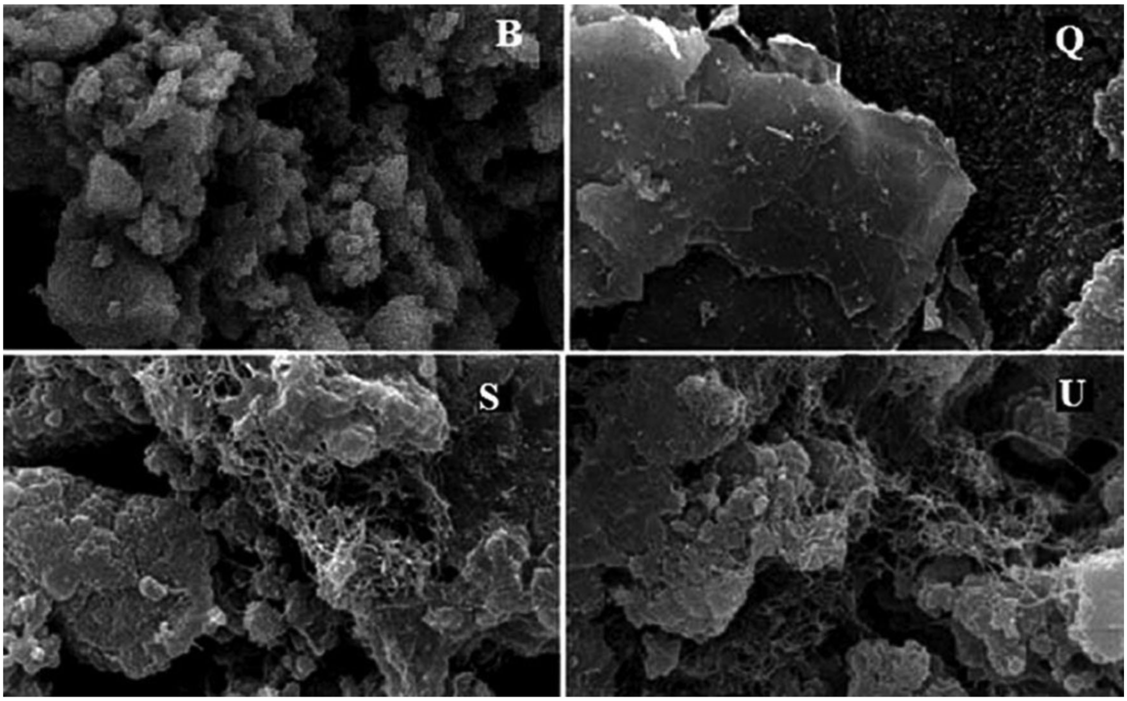

Figure 4. SEM images of polymer samples (B,Q, S,U from Table 6), magnification 15,000×.

(Figure 4). By comparing the image of sample B (polymer resulting from copolymerization without additives) to the images of samples Q, S, and U from copolymerization in the presence of the additives, it can be observed that graphene by coating the surface of the polymer and carbon nanotubes by bridging and filling the empty spaces between the polymer chains make it possible to connect the various polymer segments, and thus, to improve the thermal resistance of the polymer. On the other hand, the catalyst activity was decreased in the presence of all additives; but it was the highest for carbon nanotubes with particle diameter of 30–50 nm.

4. Conclusion

After analyzing the behavior of the polymers obtained by copolymerization of ethylene and 1-octene, the following results were obtained. In Ziegler-Natta catalyst system, by increasing the amount of 1-octene in the feed, the catalyst activity decreased. Polymers produced by the copolymerization of ethylene and 1-octene conducted at higher concentrations of comonomer showed higher levels of non-saturation than the polymers derived from ethylene homopolymerization. The melting temperature and crystallinity percent of copolymers were reduced by increasing the concentration of comonomer in the feed. In the beginning, the melting point decreasing trend was very intense, but then it showed a moderate trend. However, the percentage of crystallinity decreased in a linear trend. With increasing temperature in the study area, the catalyst activity first increased and then decreased. The best temperature was obtained at 60 °C with the highest efficiency. The viscosity average molecular weight of polymer samples decreased with increasing temperature in the range of 50–70 °C. By increasing the ethylene pressure in the range of 3–5 bar, the production increased. With increasing the ethylene pressure, the viscosity average molecular weight increased. With increasing the polymerization time from 0.5 h to 2.5 h, the catalyst activity increased in the first hour and then decreased. Preparation of ethylene/1-octene copolymer nanocomposites using graphene and carbon nanotubes was associated with catalyst activity decreasing. The thermal resistance of polymer nanocomposites increased about 10 °C relative to that of the control sample. The melting temperature and crystallinity percent of polymer nanocomposites increased compared to those of the control sample.

Acknowledgments

We are thankful of Ferdowsi University of Mashhad (FUM) and Iran Polymer and Petrochemical Institute for the technical support of this research.

Funding

This research was financially supported by the Ferdowsi University of Mashhad, Faculty of Science under Project No. 3/33224.

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