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Thermal and mechanical properties of LDPE by the effects of organic peroxides

Kamil Sirin[a]*, Ömer Cengel[b] and Murat Canli[c]

In this study, the effect of different organic peroxides on different types of low-density polyethylene (LDPE) was investigated. LDPE products like F2-21T, F5-21T, and I22-19T were mixed in different proportions with dialkyl peroxide, dibenzoyl peroxide, and dilauroyl peroxide. Melt flow rates, mechanical properties (tensile strength at yield, tensile strength at break, elongation at break, and stress-strain effect), thermal analysis (differential scanning calorimetric and thermogravimetric analysis), and scanning electron microscopy images of the prepared mixtures were examined. Cross-linking occurred in the structure of LDPE types having different molecular weight distribution by the addition of even small amounts of peroxide (e.g. 0–0.12 wt%). Copyright © 2017 John Wiley & Sons, Ltd.

Keywords: cross-linking; low-density polyethylene; organic peroxide; mechanical properties; thermal properties

INTRODUCTION

Polyethylene (PE) is an extensively used plastic material because of its valuable properties, due to its light weight, low cost, flexibility, toughness, good mechanical properties and resistance to chemicals and harsh environments, good dielectric properties, and electrical insulation.[1–3]

Polyethylene is widely used for manufacturing various containers, dispensing bottles, wash bottles, tubing, plastic bags for computer components, and various molded laboratory equipment.[4] Cross-linking is the desired process in order to accomplish these qualities, and this can be achieved by organic peroxides.[4,5]

Polyolefin chains via splitting of the C–H bonds the primary free radicals (RO·) generated by the thermal decomposition of organic peroxides, ROOR (Schema 1). In the case of PE, corresponding macroradicals is very likely to couple with another macroradical, leading a structure with long-chain branches. Because branched polymer is more compact than linear polymer at any given molecular weight, long-chain branching (LCB) is a well-known structural phenomenon in PE.[6] LCB can be incorporated directly during the synthesis, as is the case for traditional radical polymerized low-density polyethylene (LDPE) and modern metallocene catalyzed qualities, or introduction of LCB by light cross-linking of linear polyolefin in a post reactor reaction. Cross-linking is normally carried out using peroxides, radiation, or vinyl silanes. Long-chain branches are structural features that have large impact on the rheological (melt) properties.[7]

The modification of PE using organic peroxides is a method extensively used to improve their thermomechanical stability, wear, and chemical resistance.[8] The method is based on generating macroradicals that follow mainly combination reactions given rise to linkages between the chains of the polymer. Because of its role in decomposing, organic peroxides are expected to generate radicals to act like polymerization initiators and cross-linking agents for the purpose of making, modifying polymers to create a thermoset. It is known that when the polymer undergoes chain-linking, the molar mass increases with the concentration of the peroxide to reach infinitely large values.[5–14] If the peroxide concentration increases further, a molecular network or gel forms, and this phenomenon is called gelation. Beyond the gelation, the gel grows with increasing the concentration of peroxide becoming a large fraction of the total mass. The changes in molecular structure affect the semi-crystalline morphology that, together with the adopted crystallization process, determines the physical and mechanical properties of the material.[15–17]

The main objective of this article is to study the effect of organic peroxides on thermal, mechanical, and rheological properties of three different types of LDPE. For this reason, dialkyl peroxide (DAP), dilauroyl peroxide (DLP), and dibenzoyl peroxide (DBP) were added to different types of LDPE using twin screw extruder, and variations in the molecular structure were examined. Petkim's low-density grade LDPE products F2-21T, F5-21T, and I22-19T were used as the polymer matrix. They were mixed in different proportions with DAP, DBP, and DLP. Severe decline was observed in melt flow rates of F2-21T, F5-21T, and I22-19T with the addition of DAP. While DAP had the highest effect on the melt flow rates, DLP and DBP were less effective for influencing the melt flow rates. The mechanical (tensile strength at break, at yield, and elongation at break), melt flow index (MFI), hardness, morphological, and thermal properties of the samples were investigated.

* *Correspondence to: Kamil Şirin, Faculty of Sciences and Arts, Department of Chemistry, Manisa Celal Bayar University, 45040 Manisa, Turkey.*
E-mail: sirin.kamil@gmail.com

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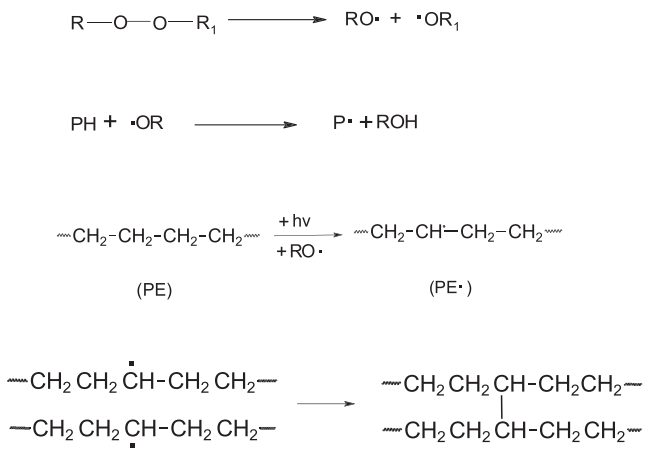
a *K. Sirin*
Faculty of Sciences and Arts, Department of Chemistry, Manisa Celal Bayar University, 45040 Manisa, Turkey

b *Ö. Cengel*
Master student at Manisa Celal Bayar University, Manisa, Turkey

c *M. Canli*
Mucur Vocational School, Department of Chemistry and Chemical Processing Technologies, Ahi Evran University, 40900 Kirsehir, Turkey



Schema 1. Chain scission and cross-linking of polyolefin.

EXPERIMENTAL

Material

Low-density polyethylene products like F2-21T, F5-21T, and I22-19T were obtained by Petkim Petrochemical Holding A.Ş. Turkey. MFI values of all LDPE samples are 2.5, 4.6, and 22.0 g 10 min^{-1} (2.16 kg, 190 ± 0.5°C), respectively. DAP, DBP, and dilauroyl peroxide (was purchased from Sigma-Aldrich Chemie GmbH, Germany) were used as organic peroxides.

Preparation of matrices

Low-density polyethylene matrices were prepared from LDPE pellets with different ratios (0 to 0.12 wt%) of DAP, DBP, and dilauryl peroxide by using twin screw extruder (Collin ZK-25T). The matrices were prepared by melting the mixed components in extruder that was set at extruder diameter: 25 mm; length to diameter ratio: 18:1; pressure: 6–8 bar; temperature scale for LDPE matrices from filing part to head was 170–220°C. And the screw operation speed was 10 rpm. All of the homopolymers totally were melted and mixed homogenously. The samples were produced that had 2 ± 0.05-mm height and 10 ± 0.1-mm width. All samples were coded given in Table 1.

Melt flow index measurements

Melt flow index measurements of the matrices were carried out on an MFI Tester-Sangyo TP401B apparatus at 230°C and under 2.16-kg weights. Five samples were cut sequentially, and their average weight was obtained. Experiments were carried out according to ASTM D-1238.

Mechanical testing measurements

Tensile testing of the matrices samples were performed at 25 ± 1°C at a crosshead speed of 50 mm min^{-1} according to ASTM D638, an Instron tensile tester (model 1114) was used.

Sample plates were prepared according to ASTM D-1238 and delayed 48–72 hr at the laboratory conditions. These sample plates were heat-molded into sheets, which were then cut into pieces and put into a 200 × 200 × 1-mm mold, and the matrices were squeezed between plates in a heating press at 230°C under 0 MPa for 2 min; 5 MPa for 2 min; 10 MPa for 2 min; 15 MPa for 1 min; and 60 MPa for 3 min.

Afterwards, the samples were cooled at room temperature. Mold was put in a hydraulic press under pressure of 150 MPa for 3 min. Sample strips for the tests were cut from the plate ASTM 638.

Five measurements were recorded for each matrix, and the average values were calculated and reported. Narrow-waist dumbbell was used at tensile test specimen (ISO/DIS 527 Type A). The averages of all values were calculated for the tensile strength at yield and break points, elongation at break, and stiffness resistance for every one recorded. Stress–strain diagrams were prepared, and results in tables were demonstrated according to Fig. 1.

Thermal analysis

The samples of approximately 10 mg were weighted in aluminum crucibles and were prepared according to ASTM D-2117. The analyses were conducted using a Shimadzu DSC-50 (Schimadzu Corporation, Tokyo, Japan). Differential scanning calorimetric (DSC) curves were obtained in the temperature range 25–200°C using heating rate of 10°C min^{-1}. DSC analyses were carried out in a Shimadzu DSC-50 thermal analyzer in nitrogen

Table 1. Nomenclature, components, and composition polymer matrices

The sample code is based on peroxide types					
Polyethylene types	Peroxide ratio (wt%)	Polymer ratio (wt%)	Dialkyl peroxide	Dilauroyl peroxide	Dibenzoyl peroxide
LDPE F2-21T	0	100	F2	F2	F2
	0.04	99.96	F2A04	F2B04	F2C04
	0.08	99.92	F2A08	F2B08	F2C08
	0.12	99.88	F2A12	F2B12	F2C12
LDPE F5-21T	0	100	F5	F5	F5
	0.04	99.96	F5A04	F5B04	F5C04
	0.08	99.92	F5A08	F5B08	F5C08
	0.12	99.88	F5A12	F5B12	F5C12
LDPE I22-19T	0	100	I22	I22	I22
	0.04	99.96	I22A04	I2B04	I22C04
	0.08	99.92	I22A08	I2B08	I22C08
	0.12	99.88	I22A12	I2B12	I22C12

atmosphere. The samples were heated from 25 to 200°C at 10°C min^{-1}, cooled down to 25°C at the same rate, and re-heated and re-cooled under the same conditions. Melting (T_m) and crystallization (T_c) temperatures and enthalpies were determined from the second scan. T_m was considered to be the maximum of the endothermic melting peak from the heating scans and T_c that of the exothermic peak of the crystallization from the cooling scans. The heat of fusion (ΔH_f) and crystallization enthalpy (ΔH_c) were determined from the areas of melting peaks and crystallization peaks.

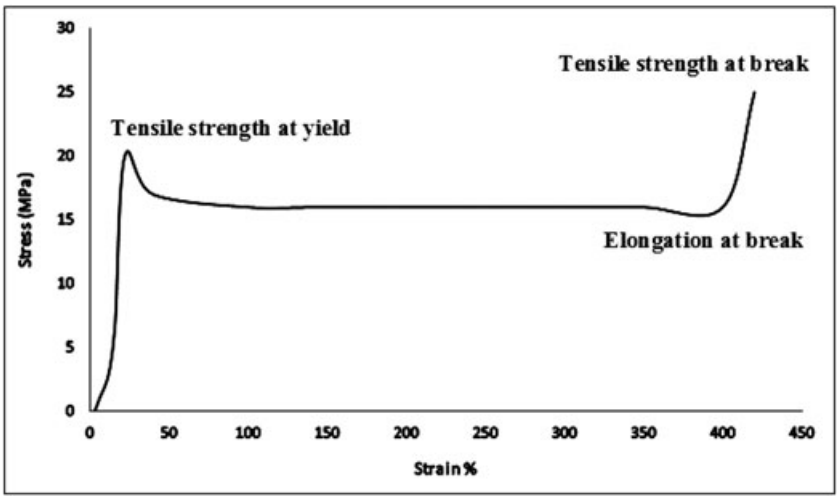


Figure 1. Design and explanation of mechanical results in stress–strain diagram.

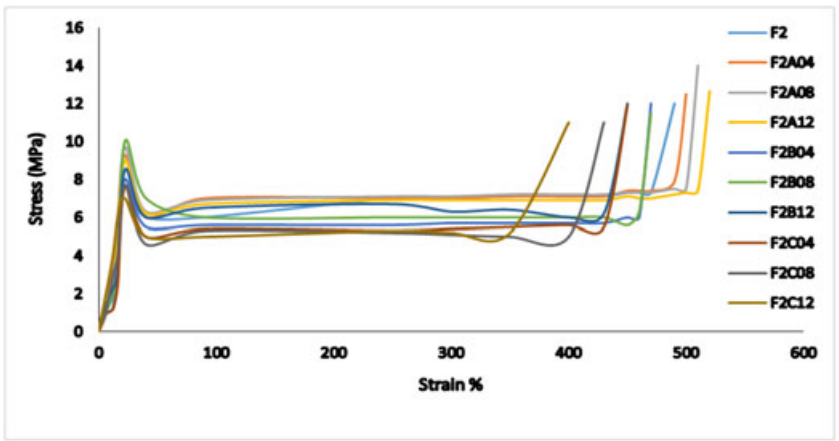


Figure 2. Typical stress–strain curves of low-density polyethylenes F2A, F2B, and F2C with different ratio. Dialkyl peroxide. (0, 0.04, 0.08, and 0.12 wt%). [Colour figure can be viewed at wileyonlinelibrary.com]

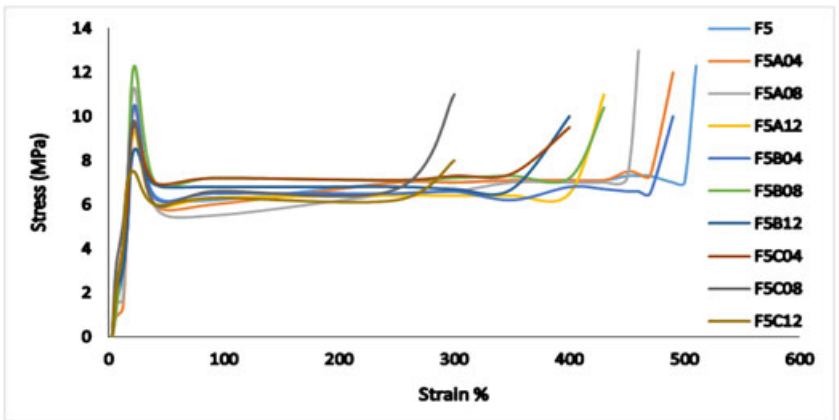


Figure 3. Typical stress–strain curves of low-density polyethylene-F5A-5C with different ratio. Dialkyl peroxide (0, 0.04, 0.08, and 0.12 wt%). [Colour figure can be viewed at wileyonlinelibrary.com]

The crystallinity of matrices was calculated through the total enthalpy method; in all calculations, the heats of fusion at equilibrium melting temperature were 293 Jg^{-1}, for LDPE crystals.[16]

$$(X_c) = \frac{\Delta H_f}{\Delta H_{crys}} x100$$

ΔH_f = Heat of fusion (J/g)

ΔH_{crys} = 100% crystal polymer crystallization energy (J/g)

(X_c) = Crystallinity$(\%)$

Scanning electron microscopy

Scanning electron microscopy (SEM) was used to examine the morphology of matrices by using a Philips XL-305 FEG e SEM. To overcome the blockages that are created by polymers during imaging, appropriate cleaning and drying, etching and staining of low contrast samples, and lightly coating and making a pathway are the steps needed to be followed. Freezing of aqueous suspension of each material with 0.1 wt% consistency at liquid nitrogen and drying the samples using freeze dryer increased the level of conditions for better SEM images on the samples.[17]

The change in melt flow rates of F2-21T samples is as follows: Dialkyl peroxide addition caused melt flow rate of F2-21T to fall from 2.45 to 0.67 g 10 min^1. DBP addition decreased the melt flow rate to 1.71 g 10 min^1. DLP addition had only a slight effect and changed melt flow rate to 2.43 g 10 min^1.

The change in melt flows rates of F5-21T samples is as follows: Dialkyl peroxide addition caused melt flow rate of F5-21T to fall from 4.47 to 0.80 g 10 min^1. DBP addition decreased the melt flow rate to 2.62 g 10 min^1. DLP addition shifted the melt flow rate to 4.14 g 10 min^1.

Dialkyl peroxide caused the melt flow rate of I22-19T to shift from 19.12 to 6.49 g 10 min^1. DBP changed melt flow rate to 16.53 g 10 min^1. DLP again did not have much effect and only decreased the melt flow to 18.04 g 10 min^1.

Dialkyl peroxide seems to be the most effective of the organic peroxides on melt flow rates of LDPE samples.

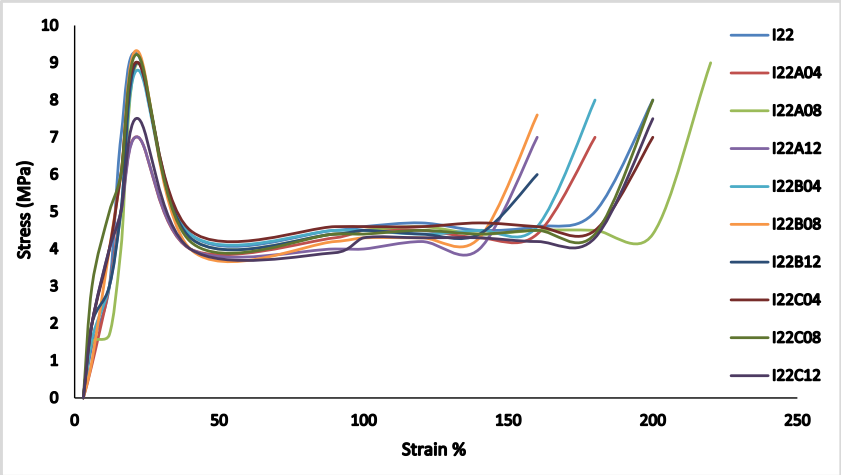


Figure 4. Typical stress–strain curves of low-density polyethylene-I22A-C with different ratio. Dialkyl peroxide (0, 0.04, 0.08, and 0.12 wt%). [Colour figure can be viewed at wileyonlinelibrary.com]

Table 2. Melt flow index values of the samples

LDPE Types	Peroxide ratio (wt%)	Melt flow index (g 10 min^{-1}) DAP	DLP	DBP
F2-21T	0	2.45 ± 0.01	2.45 ± 0.01	2.45 ± 0.01
	0.04 ± 0.01	2.30 ± 0.01	2.40 ± 0.01	2.44 ± 0.01
	0.08 ± 0.01	1.35 ± 0.01	2.47 ± 0.01	2.24 ± 0.01
	0.12 ± 0.01	0.67 ± 0.01	2.43 ± 0.01	1.71 ± 0.01
F5-21T	0	4.47 ± 0.01	4.47 ± 0.01	4.47 ± 0.01
	0.04 ± 0.01	4.43 ± 0.01	4.39 ± 0.01	3.64 ± 0.01
	0.08 ± 0.01	2.60 ± 0.01	4.22 ± 0.01	3.68 ± 0.01
	0.12 ± 0.01	0.80 ± 0.01	4.14 ± 0.01	2.62 ± 0.01
I22-19T	0	19.12 ± 0.01	19.12 ± 0.01	19.12 ± 0.01
	0.04 ± 0.01	12.68 ± 0.01	18.83 ± 0.01	19.51 ± 0.01
	0.08 ± 0.01	10.90 ± 0.01	16.79 ± 0.01	13.96 ± 0.01
	0.12 ± 0.01	6.49 ± 0.01	18.04 ± 0.01	16.53 ± 0.01

DAP, dialkyl peroxide; DBP, dibenzoyl peroxide; DLP, dilauroyl peroxide; LDPE, low-density polyethylene.

Thermogravimetric analysis

The thermogravimetric analysis was performed with a Perkin Elmer Pyris 1. Heating rate of 10°C $min^{-1}$was used. The sample weight was about 10 mg, and all experiments were carried out under a dynamic flow of nitrogen or air atmosphere (200 mL min^{-1}).

RESULT AND DISCUSSIONS

Mechanical analysis results

Figures 2–4 show the stress versus strain curves for LDPE-F2, LDPE-F5, and LDPE-I22 composites for a range of peroxide DAP volume fractions. Yield strength values tend to increase between 0 and 0.08 wt% peroxide ratios but decrease by further peroxide addition from 0.08 to 0.12 wt% by weight.

This trend can be explained as follows. Because of the cross-linking of LDPE structure by organic peroxides, LCB causes the molecular weight of the polymer to increase. However, further addition of organic peroxides results a rise in intermolecular interactions rather than intermolecular interactions.

Investigating "tensile strength at break results" reveals that by rising DAP and DBP ratio "the tensile strength at break values" increase. However, DLP addition has negative effect on tensile strength at break.

It can be concluded that the composite samples tend to reach the upper yield point (ultimate stress). Then the samples extend elastically until they reach the lower yield point, and finally, they draw till it breaks.[18–20]

Melt flow index analysis

Table 2 summarizes that the melt flow rates of the matrices vary by increasing amount of peroxide. Even a small amount of organic peroxide causes cross-linking in the structure of LDPE types having different molecular weight distributions.[18,21–23]

The radicals that are formed by thermal decomposition of organic peroxides are very reactive due to the unpaired electron in their structure. These active radicals abstract hydrogen atoms from the polymer chains and lead to the formation of macroradicals. The tendency of macroradicals to cross-link polymer molecules causes the viscosity of the samples to increase and melt flows to decrease.

The melt flow rates of F2-21T, F5-21T, and I22-19T seriously declined by DAP addition. However, melt flow rates of the same samples did not decrease much with DLP and DBP addition.

Thermal analysis results

Differential scanning calorimetric results

Thermal behavior of LDPEs with/without peroxides were examined by melting temperatures, crystallization temperatures, melting and crystallization energies, and crystallinity (%). The results were shown in Table 3.

According to Figs 2–4 and Table 4, DSC analyses of the samples show similar behavior with mechanical analyses.

According to Table 4, DAP, DLP, and DBP addition did not have much effect on melting point T_m and crystallinity point T_c of F2-21T samples (T_m: 106–107°C; T_c: 91–93°C). However, enthalpies of fusion (ΔH_f), enthalpies of crystallinity (ΔH_c), and crystallinity ratios (X_c) have been improved (ΔH_f: 95.41–103.52 j.g^{-1}, ΔH_c: 75.07–79.57 j.g^{-1}, X_c: 32.56–35.33) between 0 and 0.08 wt% peroxide ratio but declined when the ratio got higher to 0.12 by wt% (ΔH_f: 103.52–100.98 j.g^{-1}, ΔH_c: 79.57–72.07 j.g^{-1}, X_c: 35.33–34.46).

The same is valid for F5-21T. Adding DAP, DLP, or DBP in F5-21T sample did not cause much variation in melting and crystallization temperatures (T_m: 106–107°C; T_c: 91–93°C). However, the fusion and crystallization enthalpies and crystallization ratios increased up to 0.08 wt% peroxide ratio (ΔH_f: 84.33–92.25 j.g^{-1}; ΔH_c: 67.86–72.68 j.g^{-1}; X_c: 28.78–31.48) but declined over 0.08 by wt% (ΔH_f: 92.25–91.01 j.g^{-1}), (ΔH_c: 72.68–68.30 j.g^{-1}), (X_c: 31.48–31.06).

Melting point and crystallization point of LDPE I22-19T samples did not change much either by DAP, DLP, or DBP addition (T_m: 104–105°C; T_c: 90–91°C) (Figs 5 and 6). Fusion enthalpies, crystallinity enthalpies, and crystallinity ratios of the samples decreased up to 0.04 wt% peroxide ratio (ΔH_f: 91.21–90.83 j.g^{-1}; ΔH_c: 74.43–67.78 j.g^{-1}; X_c: 35.15–29.46), rose by 0.08 wt% (ΔH_f: 90.83–90.89 j.g^{-1}; ΔH_c: 67.78–79.99 j.g^{-1}; X_c: 29.46–35.86) but declined again by 0.12 wt% peroxide ratio (ΔH_f: 90.89–90.18 j.g^{-1}; ΔH_c: 79.99–71.36 j.g^{-1}; X_c: 35.86–30.68).

Table 3. DSC Analysis of LDPE samples

	Melting (from second heating scans)		Crystallization (from second cooling scans)		
Sample code	T_m (°C)	ΔH_f (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})	X_c (%)
F2	107.47	95.41	93.07	75.07	32.56
F2A04	106.98	96.74	93.02	75.18	33.02
F2A08	107.12	103.52	93.56	79.57	35.33
F2A12	106.83	100.98	93.34	72.07	34.46
F2B04	106.95	99.08	93.76	67.40	33.82
F2B08	107.51	103.03	93.20	76.43	35.16
F2B12	107.00	100.87	93.71	74.72	34.43
F2C04	107.34	102.02	93.17	73.68	34.82
F2C08	106.90	104.99	93.71	78.40	35.83
F2C12	107.68	102.43	93.35	72.39	34.96
F5	107.12	84.33	92.42	67.86	28.78
F5A04	106.45	86.59	92.60	68.54	29.55
F5A08	106.15	92.25	92.70	72.68	31.48
F5A12	106.13	91.01	92.58	68.30	31.06
F5B04	107.03	89.20	92.64	72.29	30.44
F5B08	106.17	98.32	93.06	76.20	33.56
F5B12	106.98	91.08	92.55	72.70	31.09
F5C04	106.68	99.64	93.00	75.29	34.01
F5C08	106.71	100.23	92.99	77.03	34.21
F5C12	106.52	85.70	93.02	70.74	29.25
I22	104.63	102.98	91.21	74.43	35.15
I22A04	104.83	86.31	90.83	67.78	29.46
I22A08	104.31	105.06	90.89	79.99	35.86
I22A12	104.68	89.88	90.18	71.36	30.68
I22B04	104.83	90.50	91.18	71.69	30.89
I22B08	104.95	106.57	90.91	76.97	36.37
I22B12	105.50	99.29	90.33	73.66	33.89
I22C04	104.83	79.54	90.84	70.00	27.15
I22C08	104.98	100.47	91.21	77.04	34.29
I22C12	104.62	92.72	91.22	69.76	31.65

DSC, differential scanning calorimetric; LDPE, low-density polyethylene.

Table 4. TGA data of LDPE sample with peroxide

		Mass loss (%)			Residue weight percentage			
Sample code	Conversation (%)	T_i (°C)	T_{max} (°C)	T_f (°C)	400°C	450°C	500°C	Char yield (%w_f)
F2	0.03–99.70	402.00	456.00	481.00	0.90	48.20	99.70	0.03
F2A04	0.02–99.80	398.00	461.00	493.00	1.10	44.60	99.80	0.02
F2A08	0.03–99.70	411.00	463.00	488.00	0.10	42.80	99.70	0.03
F2A12	0.01–99.90	419.00	469.00	494.00	0.01	40.70	99.90	0.01
F2B04	0.02–99.80	362.00	471.00	491.00	25.0	36.50	99.80	0.02
F2B08	0.03–99.70	413.00	469.00	494.00	0.01	39.80	99.70	0.03
F2B12	0.01–99.90	381.00	460.00	486.00	20.50	44.90	99.90	0.01
F2C04	0.02–99.80	387.00	459.00	490.00	18.60	46.70	99.80	0.02
F2C08	0.01–99.90	363.00	448.00	475.00	24.70	49.50	99.90	0.01
F2C12	0.02–99.80	413.00	459.00	485.00	0.10	44.60	99.80	0.02
F5	0.01–99.90	405.00	456.00	479.00	0.10	47.60	99.90	0.01
F5A04	0.03–99.70	400.00	458.00	468.00	0.99	48.20	99.70	0.03
F5A08	0.02–99.80	413.00	459.00	483.00	0.10	47.90	99.80	0.02
F5A12	0.01–99.90	407.00	473.00	477.00	0.10	45.10	99.90	0.01
F5B04	0.02–99.80	350.00	444.00	480.00	40.5	67.20	99.80	0.02
F5B08	0.01–99.90	344.00	443.00	470.00	43.5	68.50	99.90	0.01
F5B12	0.01–99.90	390.00	456.00	475.00	12.0	48.80	99.90	0.01
F5C04	0.01–99.90	413.00	459.00	483.00	0.10	48.10	99.90	0.01
F5C08	0.01–99.90	411.00	468.00	474.00	0.10	45.90	99.90	0.01
F5C12	0.01–99.90	400.00	458.00	468.00	0.99	48.60	99.90	0.01
I22	0.02–99.80	391.00	454.00	481.00	3.60	49.50	99.80	0.02
I22A04	0.03–99.70	418.00	472.00	490.00	0.09	46.80	99.70	0.03
I22A08	0.09–99.10	423.00	473.00	496.00	0.08	45.70	99.10	0.09
I22A12	0.08–99.20	420.00	470.00	497.00	0.08	46.90	99.20	0.08
I22B04	0.03–99.70	417.00	472.00	496.00	0.08	46.50	99.70	0.03
I22B08	0.03–99.70	422.00	472.00	495.00	0.08	46.40	99.70	0.03
I22B12	0.02–99.80	396.00	457.00	481.00	0.96	48.70	99.80	0.02
I22C04	0.02–99.80	414.00	460.00	486.00	0.10	47.90	99.80	0.02
I22C08	0.02–99.80	407.00	458.00	489.00	0.10	47.70	99.80	0.02
I22C12	0.02–99.80	413.00	467.00	483.00	0.10	46.80	99.80	0.02

T_i, initial decomposition temperature based upon 1% weight loss.
T_{max}, decomposition temperature based upon 50% weight loss.
T_f, decomposition temperature based upon 99% weight loss.
LDPE, low-density polyethylene; TGA, thermogravimetric analysis.

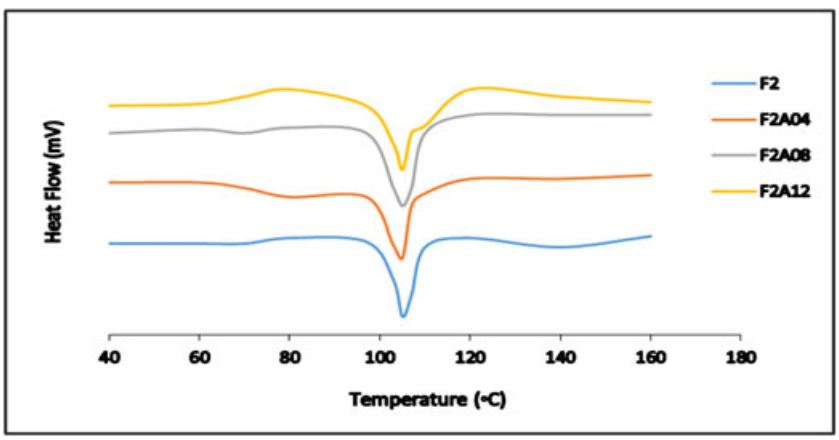


Figure 5. Differential scanning calorimetric melting curve of low-density polyethylene F2 with different ratio. Dialkyl peroxide (0, 0.04, 0.08, and 0.12 wt%). [Colour figure can be viewed at wileyonlinelibrary.com]

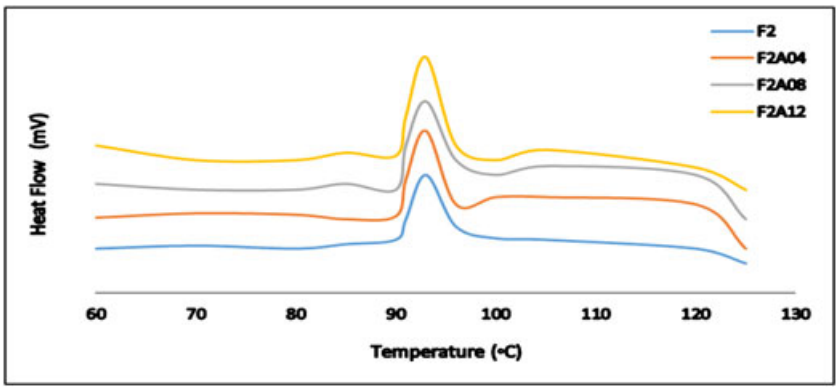
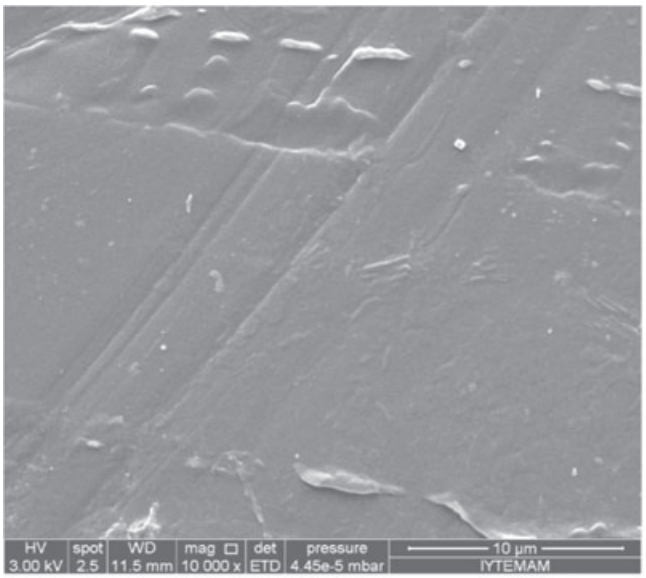
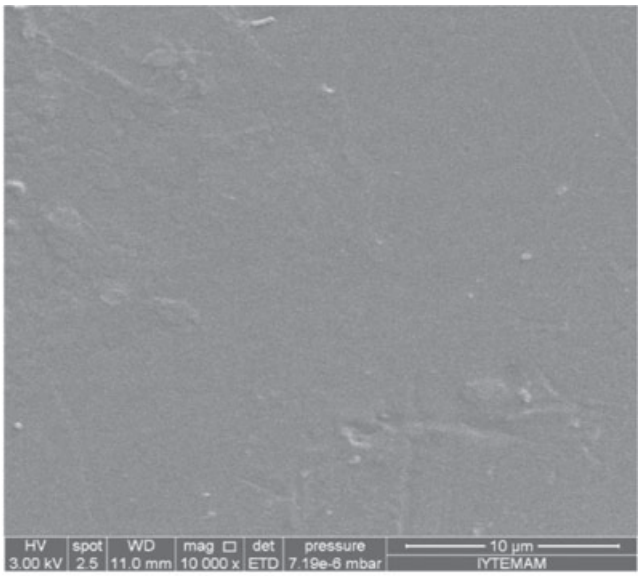


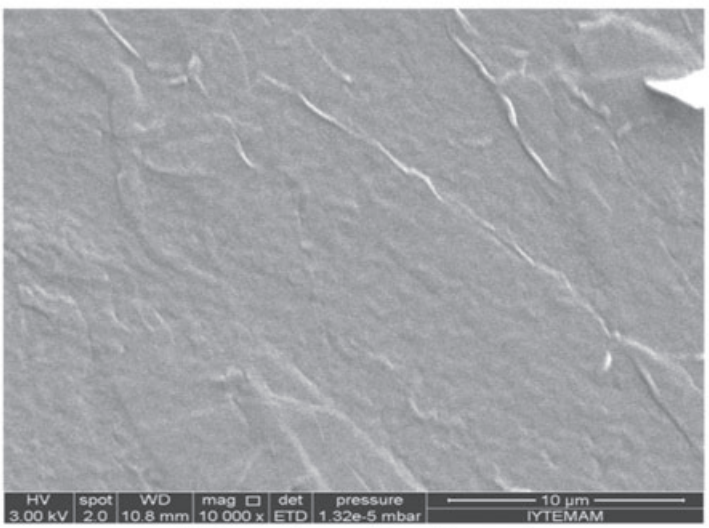
Figure 6. Differential scanning calorimetric crystallization curve of low-density polyethylene F2 with different ratio. Dialkyl peroxide (0, 0.04, 0.08, and 0.12 wt%). [Colour figure can be viewed at wileyonlinelibrary.com]



a) Dialkyl peroxide with sample



b) Dilauroyl peroxide with sample



c) Dibenzoyl peroxide with sample

Figure 7. Scanning electron microscopy images of low-density polyethylene F2-21T (peroxide ratio: 0.08 wt%).

In PE, a rapid initial drop is noticed during peroxide cross-linking, and the test results confirmed this trend. On the basis of molecular weight, LCB increases, it causes shrinkage in the polymer molecule. The shrinkage causes an increase in intra-molecular interactions rather than intermolecular ones and leads to a kind of folding in LDPE molecule.

Thermogravimetric analysis results

Thermal stability (or heat resistance) is defined as the resistance of the material against temperature, or in another word, it is the maximum temperature (decomposition temperature) that the material retains its useful properties.

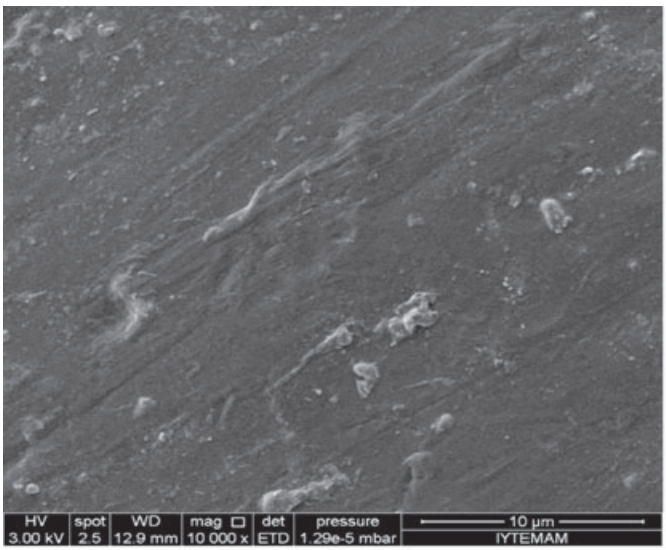
Thermogravimetric analysis results of samples are summarized in Table 4. The peroxide is added in general based on the type of change observed mass loss.

According to the thermal stability data in Table 4; F2A08, F2B08, F2C04, F2C08, F5A08, F5C08, I22B08, and I22C08 samples were observed to have the highest heat resistance.

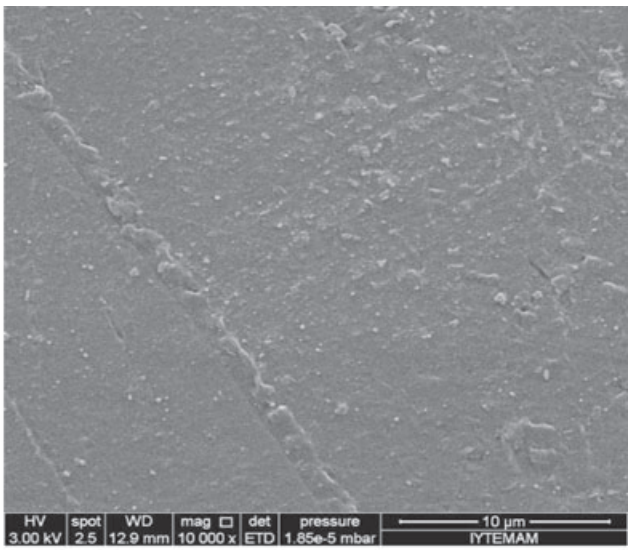
Especially, 0.08 wt% ratios became prominent in relation to thermal stability of the samples. This result showed that the ideal peroxide (DAP, DLP, and DBP) ratio for the stability of LDPE F2-21T, F521T, and I22-19T was 0.08 wt%. Other mechanical and DSC analyses confirmed these results.

Scanning electron microscopy images

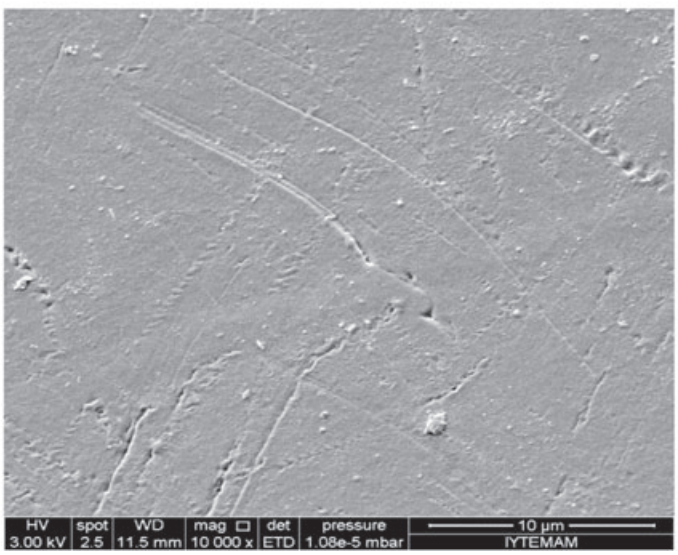
The SEM images of the samples were taken in Izmir Institute of Technology by Philips XL-305 FEG model scanning electron microscope. The best results were detected in the 10,000× magnified images. In order to understand the morphologies of PE matrices, it was focused on the fracture surfaces in SEM



a) Dialkyl peroxide with sample

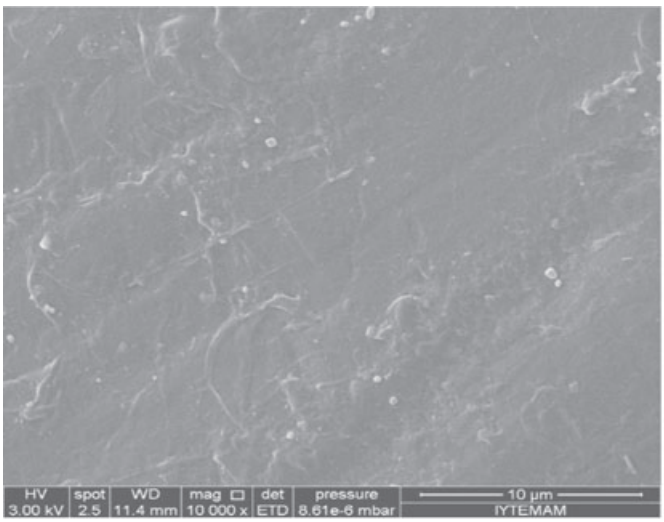


b) Dilauroyl peroxide with sample

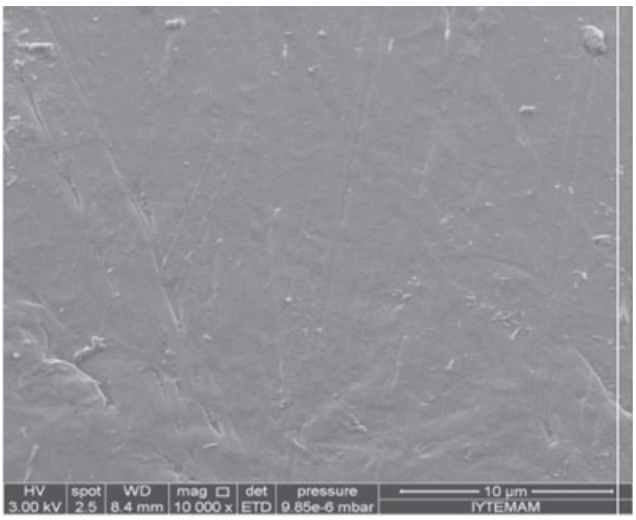


c) Dibenzoyl peroxide with sample

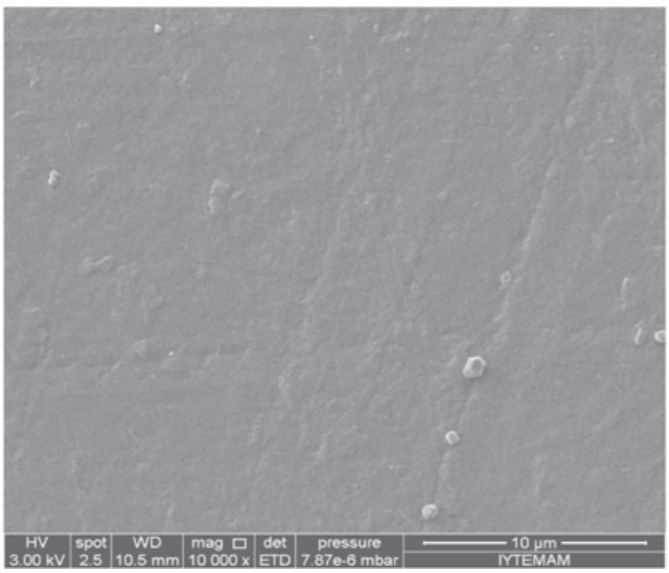
Figure 8. Scanning electron microscopy images of low-density polyethylene I22-19T (peroxide ratio: 0.08 wt%).



a) Dialkyl peroxide with sample



b) Dilauroyl peroxide with sample



c) Dibenzoyl peroxide with sample

Figure 9. Scanning electron microscopy images of low-density polyethylene F5-21T (peroxide ratio: 0.08 wt%).

images. The optimum peroxide ratio has been found to be 0.08% by weight, so only the samples having the optimum ratio were observed. The images are shown in the succeeding figures.

The SEM images of LDPE F2-21T with 0.08 wt% peroxide ratio are seen in Fig 7. The images share similarities with the ones in Fig 8. There are many interactions in DAP and DBP samples than DLP samples.

In Fig 8, the SEM images of LDPE I22-19T with 0.08 wt% peroxide ratio can be observed. The peroxides are clearly seen to affect the surface of the polymer in case of DAP and DBP samples. There is not much interaction in the samples with DLP.

Figure 9 shows the SEM images of LDPE F5-21T with 0.08 wt% peroxide ratio. Unlike the former figures, the interactions of DLP and DAP samples show dominance. DBP seems to have lesser effect on LDPE F5-21T.

Examination of SEM images of the samples revealed that DAP had the best dispersion in the polymer matrix. In terms of uniform distribution, DBP took the place after DAP. The minimum interaction between the polymer and the peroxide was observed in DLP samples.

CONCLUSION

F2-21T, F5-21T, and I22-19T samples of LDPE produced in Petkim petrochemical with different ratios (0–0.12 wt%) of DLP, DAP, and DBP were added. Some polyolefin are prone to chain scission reactions in the presence of free radicals accordingly. In terms of data given in the study, the effect of cross-link with melt flow rates, thermal, mechanical, and rheological changes that occur in samples are as follows:

- The most affected polymers by peroxide are, respectively, I22-19T > F5-21T > F2-21T.
- Among peroxides, the most effective are, respectively, DAP > DBP > DLP.

- The melt flow rates of F2-21T, F5-21T, and I22-19T seriously declined by DAP addition.

Activity rates of peroxides and types of PE in terms of the change in mechanical and thermal properties, those products can be effectively used in many areas of industry.

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