

# Influence of thermal oxidation on surface and thermo-mechanical properties of polyethylene

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**Abstract** Blown low density polyethylene (LDPE) films added with oxo-biodegradable additive containing pro-oxidant were subjected to thermo-oxidation in an oven at 70 °C for varying time periods. The changes in mechanical and surface properties were studied using tensile strength, elongation at break, wettability, surface morphology using SEM, surface topology by AFM, functional groups by FTIR spectroscopy, absorbance spectra by UV-Vis spectroscopy. The thermally aged films with pro-oxidant additive added polyethylene (PE) exhibited a higher level of oxidation as revealed by increase in their carbonyl index than the pristine

PE. In addition to it, the DSC melting behavior showed a slight increase in crystallinity (%C) and melting temperature ( $T_m$ ) of the polymer containing oxo-biodegradable additive. The SEM micrograph reveals the increase in the size of cracks and grooves, according to the increase in the concentration of pro-oxidant additive. The surface roughness also supports the same through AFM image. The increase in the wettability and surface free energy of the thermally aged samples were attributed to the formation of hydrophilic groups on the polymer surface by thermo-oxidation. The pro-oxidant additive offers a new insight into the thermo-oxidation strategy for PE and can be widely used in packaging industry.

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## Introduction

The wide usage of polyethylene (PE) in packaging industry has become inevitable owing to its advantage of flexibility, physical strength, durability and frugality. Polyethylene plays a vital role in packaging food stuff, preparing tetrapacks, candy wafers, shampoo sachets, motor pumps and other equipment sealing covers, etc. [1]. Over a period of usage it has become one among the materials of municipal garbage. Aerobic composting is being supported as a major effort to dispose waste. Still landfill remains the major waste management method globally [2, 3]. In a metropolitan area like Chennai in India, about 3,400 tons of plastic waste is generated every day, of which 35 to 40 tons consist of plastic bags [4]. PE is relatively inert due to its hydrophobic chains and high molecular weight. From earlier studies, it is evident that polyethylene biodegrades

less than 0.5% in 100 years and about 1% if pre-exposed to sunlight for about 2 years [5]. PE represents a significant percentage of municipal waste. The cost of collecting, cleaning and sorting the entire post-consumer PE is high, and the market for mechanically recycled PE is limited.

Researchers adopted many new methods to facilitate the environmental abiotic-oxidation and biodegradation of PE by polymer copolymerization [6], grafting and blending with oxo-biodegradable additives [7, 8] or direct incorporation of natural biodegradable polymers, such as starch [9, 10]. Oxo-biodegradable additives consisting of parts per million levels of transition element/metal organic salts added to conventional plastics like polyethylene (PE) and polypropylene (PP), are used to make polyolefin plastic degrade rapidly when it reaches end-of-use. Iron acts as a “delayed action” photo-sensitizer [11] activated by UV light exposure, whereas Ni, Cr (IV), Co and Cu [12–14] are sensitive to thermal activation. The transition metals can exhibit variable oxidation states and it is responsible for their pro-oxidant nature. The central metal responsible for the pro-oxidative ability usually belongs to the first transition series like manganese, iron and cobalt as stearates, all of which have the capacity to exist in both +2 and +3 oxidation states [12]. The manufacturers normally don’t reveal the identity of the pro-oxidant additive(s) used in commercial oxo-biodegradable additives. But the modifications they induce in the polymer’s functional behaviour are quite interesting. The additives are probably based on transitional metals, capable of yielding two metal ions differing in the oxidation number by one unit [15]. The pro-oxidants help to generate free radicals, which react with molecular oxygen to produce peroxides, hydro-peroxides and lead to PE decomposition under light and heat conditions leading to the formation of ketones and olefins [16, 17]. It facilitates chain end scission and random scission of PE via classical free radical chain reaction [18, 19].

The present study was carried out to investigate the changes in the mechanical, thermal and surface of modified LDPE films upon the introduction of hydrophilic groups on the polymer surface by thermal-oxidation as influenced by a commercially available oxo-biodegradable additive.

## Experimental

### Materials

The commercially available oxo-biodegradable additive (“Biodegradable Masterbatch™”) containing pro-oxidant additive cobalt (III) stearates (0.3% w/w), supplied from K K Polycolor India Ltd, was incorporated in varying ratio

with the LDPE, to prepare modified LDPE films. Commercial grade low density polyethylene (24FSO40) of MFI=1, was used for the preparation of polyethylene films.

### Preparation of biodegradable PE film

Thin films ( $50 \pm 01 \mu\text{m}$ ) were prepared by mixing varying amounts of (10 and 20%) of oxo-biodegradable additive with LDPE in a film blowing machine using an extruder (Gurusharan Polymer Make) with a 40 mm screw of L:D:: 26:1 attached to a film blowing die. A spiral die with a dia of 4 in and a die gap of 0.5 mm was employed for this purpose. Films of uniform thickness were prepared by maintaining a constant nip roller; with a taking up the speed of 35 rpm under constant blowing. The temperature in barrel zones were maintained at 125 °C (feed zone), 135 °C (compression zone) and that of the die section was 150 °C (die zone). The films were prepared as lay flat tube of bubble size 150 mm dia.

The three samples namely, Pristine LDPE films were designated as (i) PE and films containing oxo-biodegradable additive were designated as BPE followed by a numerical suffix indicating the amount of additive added. LDPE films containing 10% and 20% oxo-biodegradable additive were designated as (ii) BPE10 and (iii) BPE20 respectively as shown in Table 1. When thermal-oxidation period exceeds up to 35 days, the BPE20 sample becomes more fragile due to temperature induced thermo-oxidation influenced by pro-oxidant in the oxo-biodegradable additive. Thus, the present study was limited to 35 days, and the thermal-oxidation behavior changes were monitored by various techniques.

### Thermal-oxidation procedure

#### Oven aging

Thermal-oxidation was carried out by placing the blown films in an air oven (Matri India, [P] Ltd, India) maintained at 70 °C for extended periods [12, 15]. Exposures were conducted in the presence of air and the PE samples were uninterrupted, (24 h per day). The samples were recovered in different time intervals.

**Table 1** Characteristics of LDPE blown film samples used in thermal-oxidation tests

Sample code	Transparency	Oxo-biodegradable additives (%)	Polyethylene (%)
PE	Transparent	–	100
BPE10	Semi-transparent	10	090
BPE20	Opaque	20	080

## Characterization techniques

### Mechanical strength test

Changes in mechanical properties like tensile strength and elongation at break were performed on LDPE films according to ASTM 882–85 using INSTRON machine (no. 6021). Films of 100 mm length and 25 mm width made as strips were subjected to a crosshead speed of 100 mm/min. The tests were taken at air-conditioned environment at 21 °C and with a relative humidity of 65%. The value is the average of five samples for each experiment.

### Fourier transformed infrared spectroscopy (FT-IR)

The surface chemical modifications which occur in LDPE films due to thermo-oxidation were investigated using FTIR spectroscopy. The FTIR spectra were recorded using a Thermo Nicolet, Avatar 370 spectrophotometer in the spectral range between 4,000 and 400  $\text{cm}^{-1}$ . The keto carbonyl index was measured from the relative intensity of the keto carbonyl bond at 1720  $\text{cm}^{-1}$  to that of the Methylene band at 1,465  $\text{cm}^{-1}$  was evaluated using the formulae;

$$\text{Keto carbonyl bond index} = \frac{I_{1720}}{I_{1465}}$$

[20]

### UV-Vis-NIR spectroscopy (UV-vis)

Thermal-oxidation induced changes in the absorption spectra characteristic of polyethylene and its blends, before and after 35 days of thermo-oxidation were determined using a JASCO V-570 UV/vis spectrophotometer in the spectral range of 190–2,500 nm.

### Contact angle and surface energy

Wettability determinations of film surfaces submitted to thermo-oxidation were performed by contact angle measurements on samples using a video based contact angle meter OCA 20 attached to a camera. The wetting liquid used was Millipore grade distilled water (liquid surface tension ( $\gamma_l$ )=72.8  $\text{mJ/m}^2$ ). The value is the average of five samples for each experiment.

Surface energy was calculated using equation of state, Schultz Method-2, using Data Physics SCA20 software (Version 2.01).

The adhesion work ( $W_{\text{adh}}$ ), a quantity related to surface wettability, was calculated using the formulae [21];

$$W_{\text{adh}} = \gamma_l (1 + \cos \theta)$$

Where  $\gamma_l$  and  $\theta$  are surface energy of testing liquid and contact angle of the LDPE

### Thermal analysis

The DSC measurements were carried out under nitrogen atmosphere using Netzsch STA 409 Simultaneous Thermal Analyzer in the heating range between  $-120$  °C and  $150$  °C (10 °C/Min). Thermal properties such as melting temperature ( $T_m$ ), and degree of crystallinity (%C) of the PE samples were calculated from DSC traces recorded. Pure indium with  $T_m=156.6$  °C and  $\Delta H_f=28.4$  J/g was used as standard.

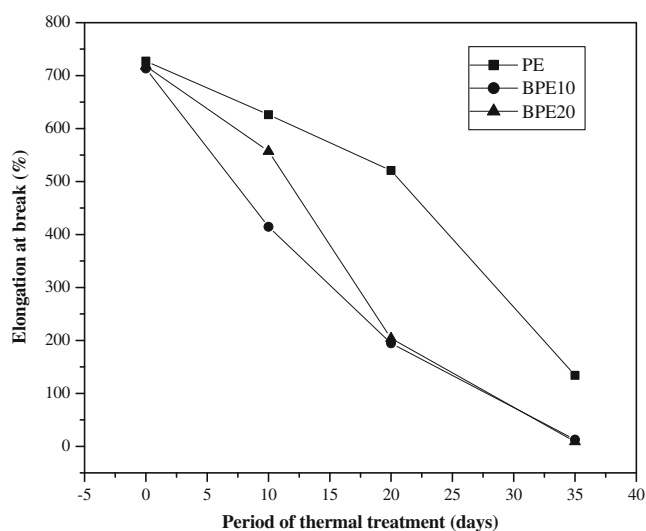
### Morphological analysis

Changes in the surface morphology due to thermo-oxidation were investigated with SEM, (JEOL Model JSM —6390LV) using a voltage of 15 kv. Photomicrographs were taken at uniform magnification of 5,000 fold and surface topography of the films were analysed by AFM (Solver P 47 PRO, Russia) using the semi-contact mode, under normal laboratory air atmosphere with the scan rate of 0.5 Hz, using single crystal silicon antimony doped probe to evaluate the change in surface topography.

## Results and discussion

### Mechanical properties

The initial elongation at break of pristine LDPE, BPE10 and BPE20 were 727.4, 713.4 and 718.1 respectively (Fig. 1). As the thermal-oxidation time increases, the pro-

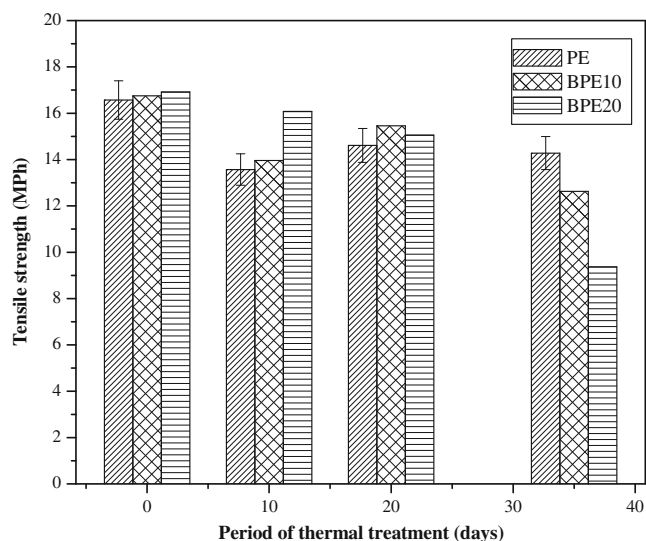


**Fig. 1** Percentage elongation of PE as a function of time for each material

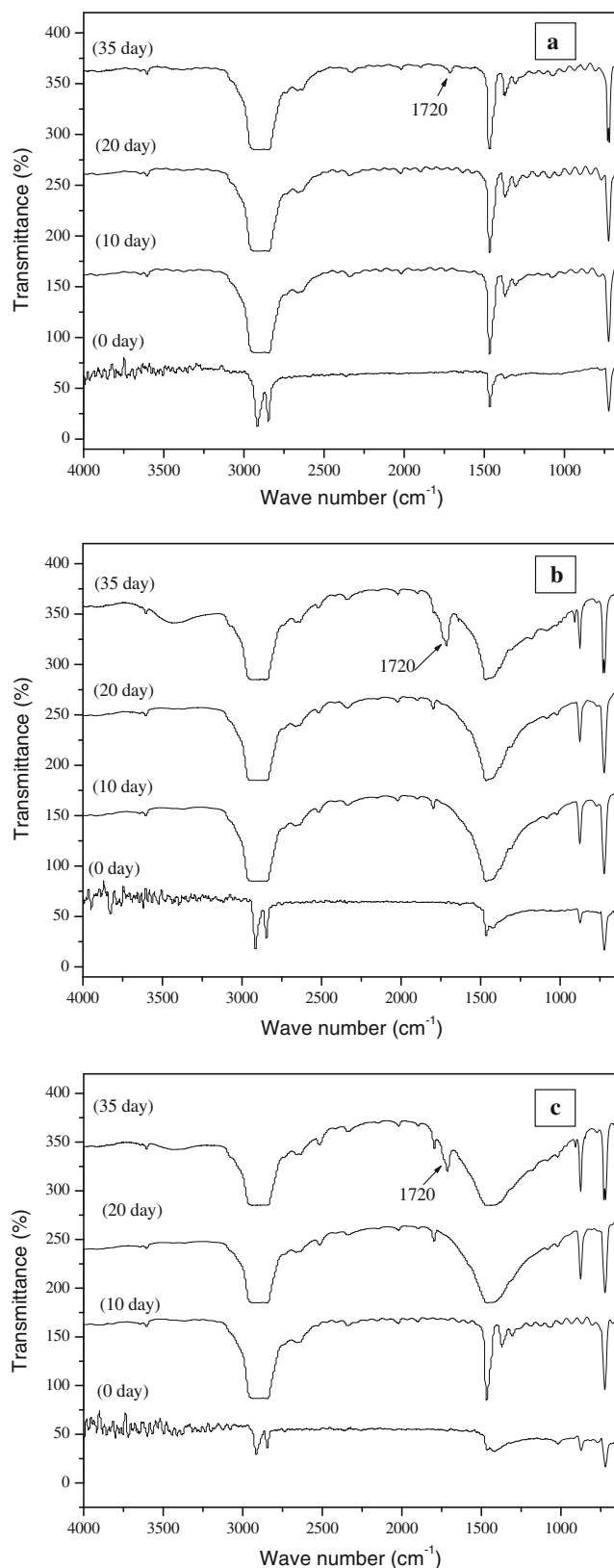
oxidant (cobalt (III) stearates) induces the chain end session [22] thereby rendering the polyethylene to lose its mechanical strength. Over a period of 35 days the pro-oxidant additive added PE retained very low value. The property of tensile strength reflects the physical strength of the polymer after a prolonged period of thermal-oxidation (Fig. 2). The BPE20 showed a deep fall from 16.9 MPa to 9.4 MPa followed by BPE10 from 16.8 MPa to 12.6 MPa and the pristine PE loses only 2 MPa from its initial strength of 16.6 MPa. Thus the visual effect of the polymer shows “brittle” in nature.

#### Structural properties - FT-IR analysis

Structural changes resulting from thermal-oxidation were investigated by recording the FTIR spectra of films in different time periods. During thermal treatment, polyethylene undergoes oxidation by producing radicals that further propagate to form peroxides. The most significant changes in the IR absorption spectra were in the carbonyl ( $1,785\text{--}1,700\text{ cm}^{-1}$ ) peak. After 20 days of thermo-oxidation an increase was observed in the intensity of the absorption band around  $1,720\text{ cm}^{-1}$ , which can be assigned to the C=O stretch of the saturated aliphatic keto-carbonyl group was observed [17]. In pristine PE (Fig. 3a), the carbonyl bond is a result of the overlap of various stretching vibration bands including those of aldehydes and/or esters and carboxylic acid groups [22]. The sharp peak of  $1,473\text{--}1,446\text{ cm}^{-1}$  resulted in CH<sub>3</sub> deformation. After 10 days of thermo-oxidation the BPE10 (Fig. 3b) shows the formation of keto carbonyl ( $1,720\text{ cm}^{-1}$ ) groups. It reaches maximum only after 35 days. The spectra also reveals the over lapping of primary and secondary amines. The influence of pro-oxidant is significant



**Fig. 2** Tensile strength of PE as a function of time for each material



**Fig. 3** FTIR spectra of (a) PE, (b) BPE10 and (c) BPE20 as a function of thermal exposure period

in spectral arrangement of BPE20 (Fig. 3c); it sharply induces the formation of saturated aliphatic keto-carbonyl functional groups upon prolonged thermo-oxidation. In the near regions, n-alkane and the secondary nitroalkane formation overlap each other causing a broadening of the peak; CH<sub>3</sub> deformation was deemed responsible for C-H scissoring [23]. The peak intensity of C=O stretching at the keto-carbonyl functional group (1,720 cm<sup>-1</sup>) and ester group (1,748 cm<sup>-1</sup>) increases with prolonged thermo-oxidation [17, 20, 22].

The extent of degradation has been quantified by calculating the CI, which is the intensity of  $\frac{I_{1720}}{I_{1465}}$  cm<sup>-1</sup> [20]. The Table 2 presents the variations in CI as a function of thermo-oxidation and the time period of exposure. It is evident that, only a small value increased in CI of pristine PE, but the BPE10 and BPE20 showed a gradual increase. The added pro-oxidant can manifest the changes in introducing the new functional groups to the BPE10 and BPE20.

#### Structural properties - UV-Vis spectral analysis

Changes in UV/vis absorption spectra of pristine and pro-oxidant added PE during exposure to thermal-oxidation are shown in Fig. 4(a, b & c). The pristine PE does not undergo major changes as BPE10 and BPE20. The observed increase of absorption was faster in PE with pro-oxidant than pristine PE. Absorbance at 200–350 nm was chosen for comparison of thermal-oxidation behaviour among the three samples. The thermally-oxidised samples tend to exhibit a red shift. But it is more evident in irradiated samples than thermally-oxidised. The changes were made because of the introduction of new carbonyl functional groups [24]. In this study, we found that the absorption increases with the increase of the concentration of pro-oxidant. Spink's et al. [25], found that since oxidation occurs in the presence of air, the carbonyl and hydroxyl compounds are formed.

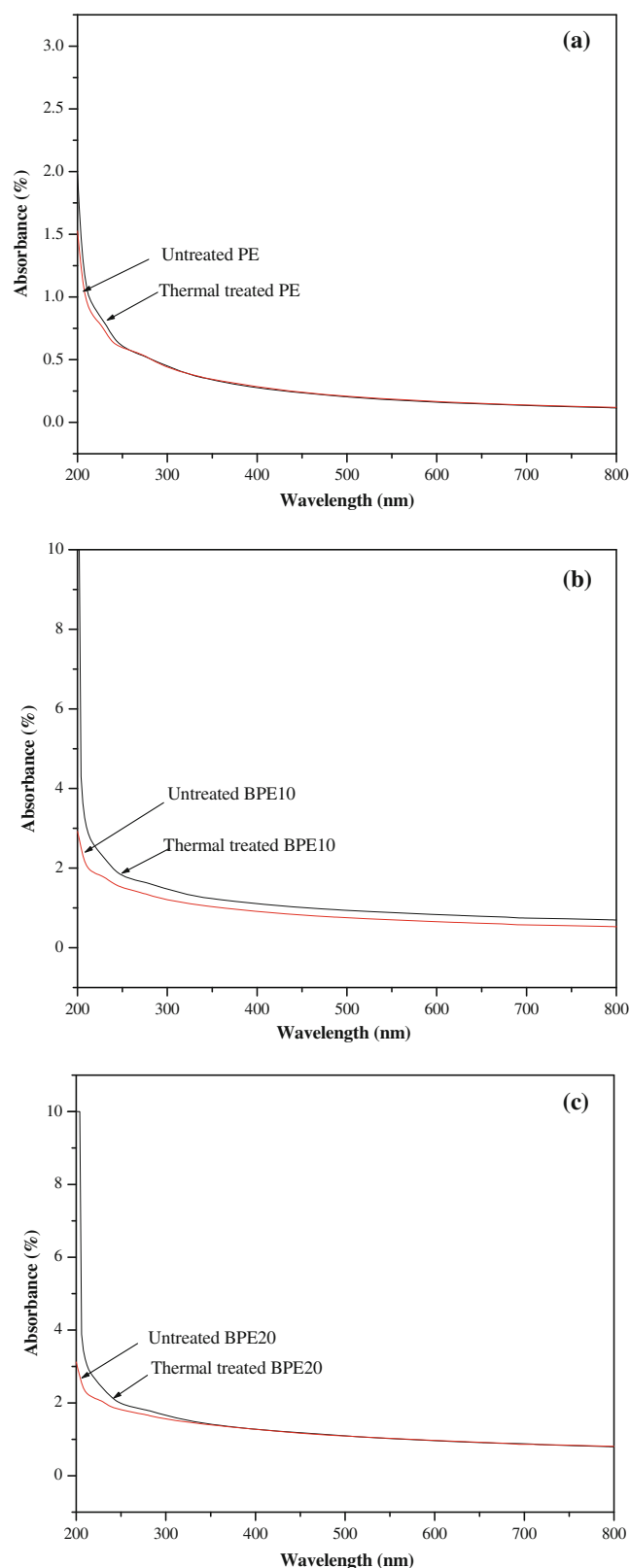
#### Surface wettability

##### Contact angle, adhesion work and surface energy measurements

The thermo-oxidation modifies the PE and BPE samples property of surface wettability. The decrease in contact

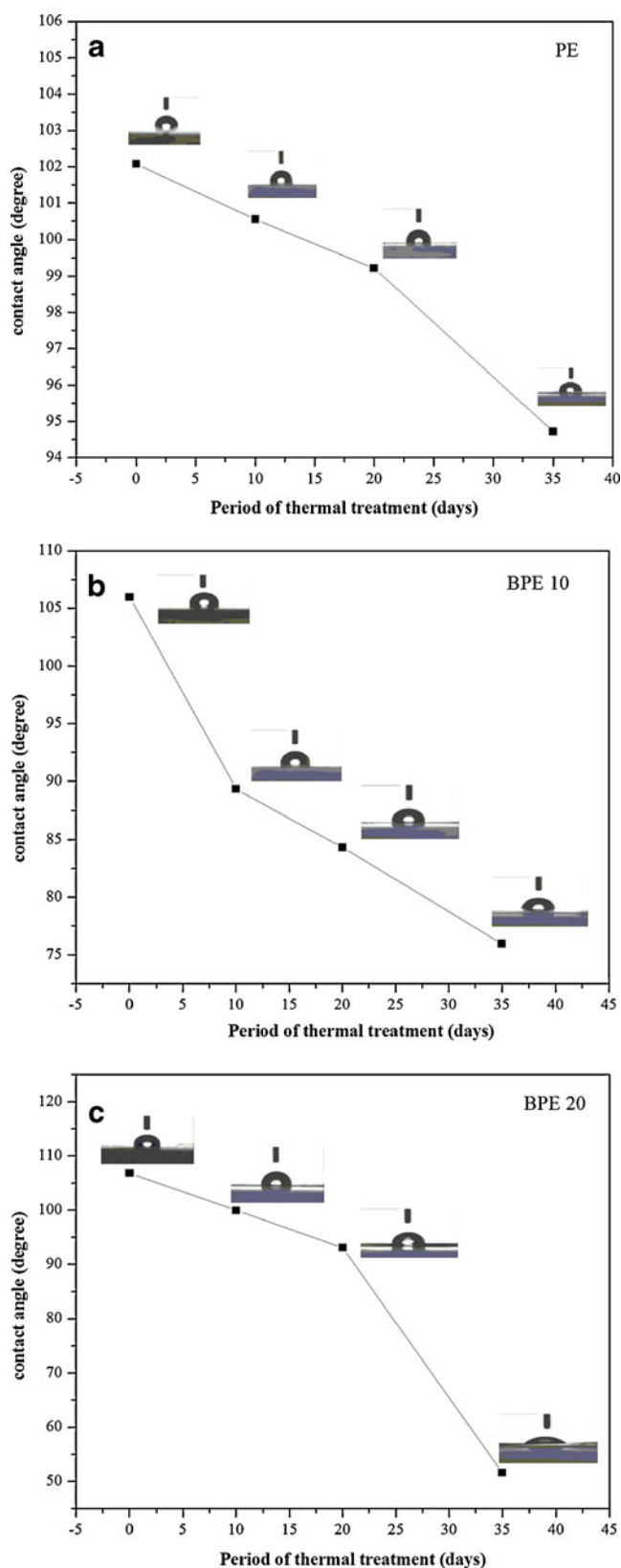
**Table 2** Influence of thermo-oxidation in increasing carbonyl index

Sample code	(Period of thermo-oxidation)			
	0 day	10 day	20 day	35 day
PE	2.00	2.08	1.48	2.10
BPE10	1.51	1.87	2.58	3.00
BPE20	1.24	1.92	2.00	4.09

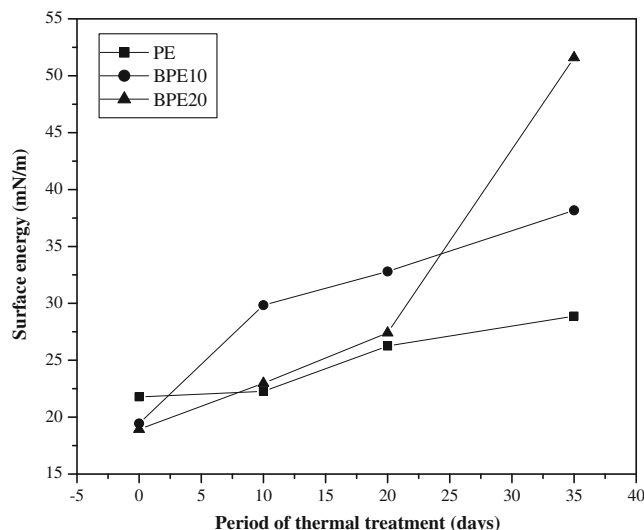


**Fig. 4** UV/Vis spectra of untreated and thermally treated (a) PE, (b) BPE10 and (c) BPE20





**Fig. 5** Comparative photographs with chart of changes in contact angle during thermo-oxidation (i) PE, (ii) BPE10 and (iii) BPE20 film as a function of various thermal exposure period



**Fig. 6** Surface energy variation profile of thermally oxidised PE and BPE films as a function of exposure time

angle (Fig. 5) indicates that the surfaces of the polymers have turned hydrophilic. The initial value of PE, BPE10 and BPE20 were 102.08, 105.98 and 106.78 were reduced to 91.22, 75.97 and 51.59 respectively. Upon the absorption of heat-energy, the components present in the pro-oxidant additive form free radicals. These species can combine with oxygen from air to generate polar groups, such as  $-\text{OH}$ ,  $\text{C}=\text{O}$ ,  $\text{COOH}$  and  $\text{COO}^-$ , on the main chain of the polymer matrix. This leads to chain end session or random session in LDPE, which alters the hydrophobic nature of the surface [26]. This phenomenon was relatively slower in PE films without a pro-oxidant additive.

The surface energy value (Fig. 6) rises as a function of thermal-oxidation period and concentration of pro-oxidant additive. The surface energies of untreated PE, BPE10 and BPE20 films were 21.78 mJ/m<sup>2</sup>, 19.44 mJ/m<sup>2</sup> and 18.97 mJ/m<sup>2</sup>, respectively. After thermo-oxidation, the surface energy of samples increases to 28.88 mJ/m<sup>2</sup>, 38.17 mJ/m<sup>2</sup> and 51.59 mJ/m<sup>2</sup>, respectively. The surface roughness is one of the important factors influencing the contact angle value. Wenzel was the first to discover the influence of surface roughness on contact angle. He

**Table 3** Effect of thermal oxidation on work of adhesion of PE, BPE10 and BPE20

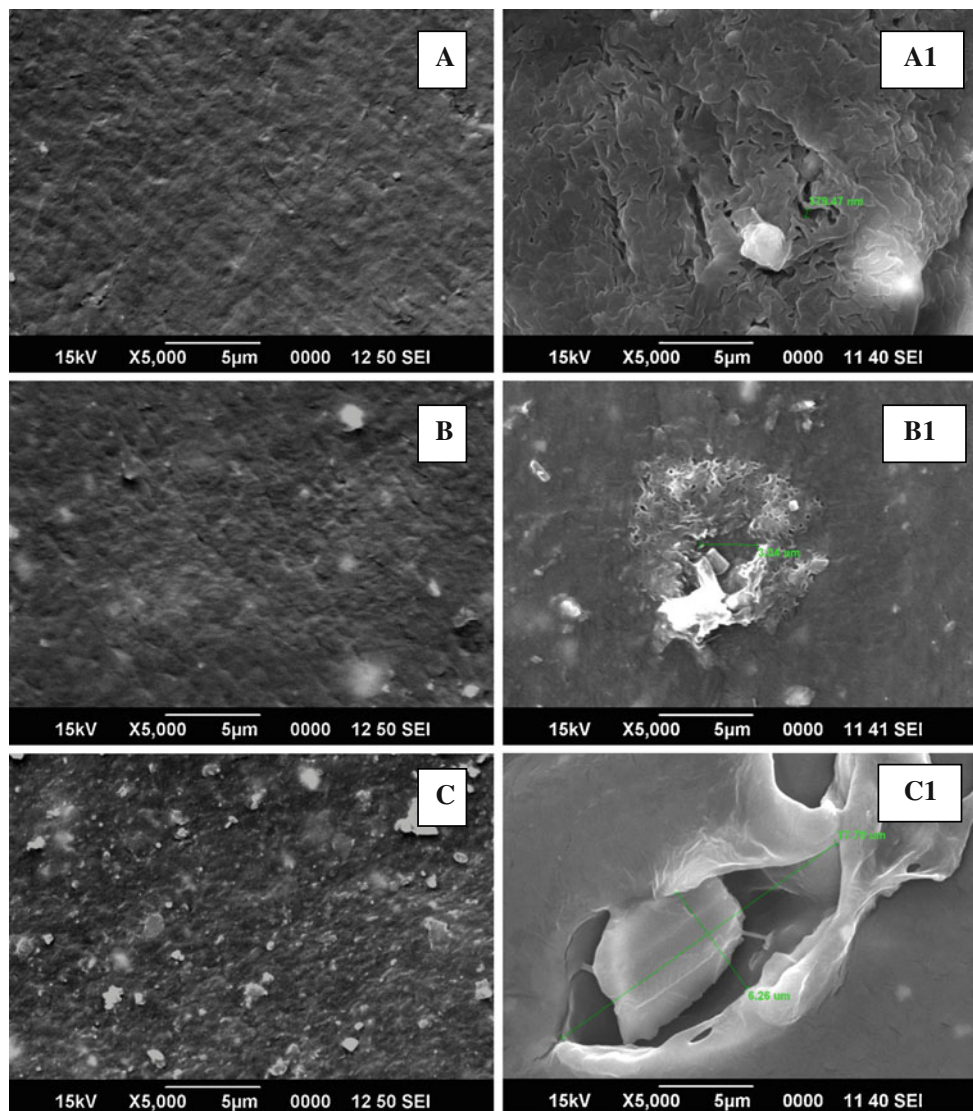
Sample	0 day	10 day	20 day	35 day
PE	57.58	59.48	63.04	71.27
BPE10	52.78	73.67	79.93	90.42
BPE20	51.58	60.28	68.87	118

**Table 4** Effect of thermal oxidation on melting and crystallization properties of PE and its blends

Sample code	% crystallinity		Melting temperature $T_m$ (°C)	
	Untreated	Treated	Untreated	Treated
PE	35.73	36.80	123.8	123.7
BPE 10	29.52	31.02	123.6	123.9
BPE 20	23.28	27.38	123.8	124.7

reported that a decrease in surface roughness produces an increase in contact angle [27]. The adhesion work ( $W_{adh}$ ) of pristine PE and LDPE with a pro-oxidant additive added is presented in Table 3. The  $W_{adh}$  was calculated from contact angle measurements with respect to water. It increases showing the modification of surface chemical groups rendering the hydrophobic nature to hydrophilic.

**Fig. 7** Comparative SEM micrographs showing surface morphology of (a) untreated PE, (b) untreated BPE10 and (c) untreated BPE20 film with 35 days thermo-oxidised PE (A1), BPE10 (B1) and BPE20 film (C1)



### Melting and crystallization behavior

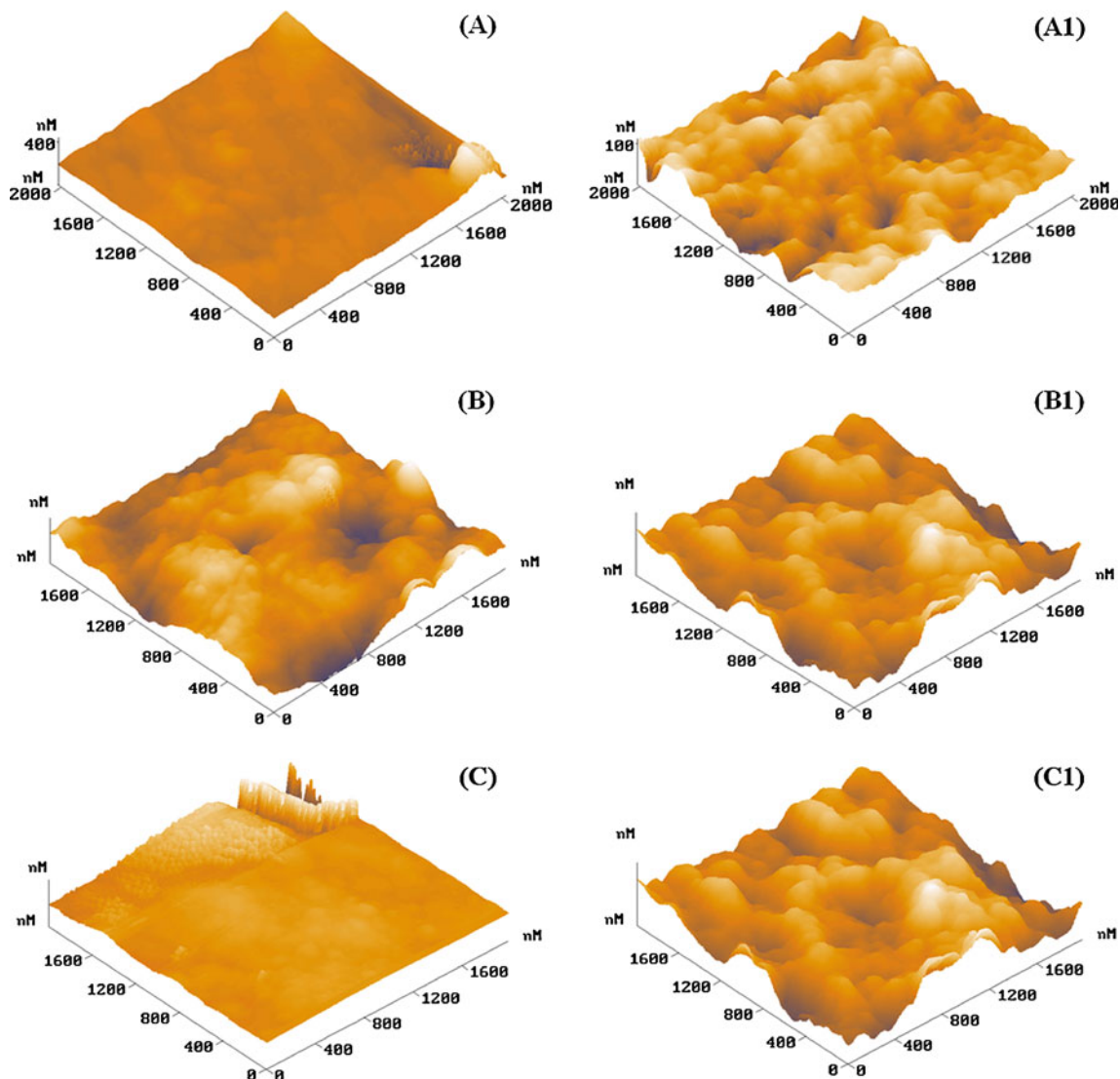
The effect of thermo-oxidation on PE and BPE sample's on the melting and crystallization behavior can be evaluated from the DSC cooling and heating curves. Table 4, reveals the parameters for melting and crystallization behavior of the samples before and after thermal aging. The samples PE, BPE10 and BPE20 show percentage crystallinity 35.73, 29.52 and 23.28 respectively. It was seen that the additive changes the crystallinity in untreated samples initially. After the thermal-oxidation the values increase to 36.8, 31.02 and 27.38 for treated PE, BPE10 and BPE20 respectively. There is not any marked (only a fractional temperature change) change in the melting peak in all the samples due to thermal aging, but the area under the melting endotherm increases upon exposure which in turn indicates the increase in crystallinity. The increase in crystallinity is an indirect result of the chain-end scission of the polyethylene in the

amorphous regions. The chain—end session allows the resulting low molecular weight segments to crystallize or act as nucleating agents for enhancing the crystallization [17]. The increase in crystallinity also contributes to the embrittlement of the films [17, 28]. It is evident that the tensile strength decreases and the cracks formed as a result of embrittlement can also be observed in SEM micrographs.

#### Surface morphological and topographical analysis: SEM and AFM

Scanning electron microscopy was used to investigate the changes in the surface morphology of thermo-treated and untreated films. Figure 7 shows the SEM micrograph of untreated PE, BPE10 and BPE20 films. Figure 7a–c shows the surface morphology as smooth, without any cracks and

free from defects. Figure 7A1 shows the formation of smaller cracks of 379 nm size with surface peeling in PE without additive. Figure 7B1 and C1 are the micrographs of 35 days thermo-oxidised BPE10 and BPE20 samples. They show the increase in size of cracks and grooves, according to the increase in the concentration of pro-oxidant additive. In Fig. 7B1 the sample BPE10 shows the cracks measuring about 3.04  $\mu\text{m}$  in diameter. However, the extent of damage was much pronounced in the sample Fig. 7C1 containing 20% additive concentration and BPE20 shows the larger groove of 17.79  $\mu\text{m}$  in diameter and the deepening of the pit is more evident. Thus the micrograph throws light on the concentration of additive that accelerates the thermo deterioration in the presence of oxygen [15, 20]. The evidence of increased crack size makes the polymer more brittle as the concentration of pro-oxidant additive increases.



**Fig. 8** Comparative AFM images showing surface topography of untreated PE (a), BPE10 (b) and BPE20 (c) film with 35 days thermo-oxidised PE (A1), BPE10 (B1) and BPE20 film (C1)



The concentration of pro-oxidant additive influences the surface modification and facilitates the surface cracks after 35 days of thermo-oxidation.

The semi-contact mode of AFM images (Fig. 8) revealed an increase in surface roughness for all the three samples after irradiation. Primarily before the irradiation the surface roughness of PE sample (Fig. 8A) was 20.58 nm and there was an increase after 35 days of thermo-oxidation in virgin PE (Fig. 8A1) 32.37 nm. The samples BPE10 and BPE20 showed a marked increase in surface roughness from 20.25 nm and 28.56 nm (Fig. 8B & C) to 59.81 nm and 155.52 nm respectively (Fig. 8B1 & C1). This shows the increased peak like pinnacle structures found more in number in BPE20 than in the other two samples. The added pro-oxidant can manifest the changes by introducing the new functional groups (such as  $-OH$ ,  $C=O$ ,  $COOH$  and  $COO^-$ ) to the BPE10 and BPE20. The results are the positive signs of the influence of increased additive concentration in accelerating the process of LDPE backbone deterioration during thermo-oxidation.

## Conclusions

The present study reveals that the PE samples with pro-oxidant additive shows a high degree of susceptibility to thermo-oxidation. But the pristine PE sample responds to a lesser extent of thermo-oxidation in comparison with pro-oxidant added PE. This is evident in BPE10 and BPE20 showing increased crystallinity. As a result of thermo-oxidation, the mechanical strength also gets reduced as the function of thermal exposure time increases. The incorporation of pro-oxidant into polyethylene initiates polymer degradation by producing free radicals which react with molecular oxygen to create peroxides and hydroperoxides which in turn promotes the chain end session of polymer backbone. Owing to the introduction of new polar groups there is a sharp increase in keto-carbonyl index was recorded in BPE20, which correlates with the other wettability parameters showing increase in surface energy and decreasing contact angle. These new polar groups contribute the change in surface property from hydrophobic to hydrophilic nature. The changes in polymer surfaces are confirmed with the modifications made in surface roughness in AFM image and the larger groove formation in SEM micrograph. The changes in surface, mechanical and thermal property due to thermo-oxidation are showing good agreement with the results of other researchers worked with pro-oxidant added PE (8,15,22). The thermo-oxidative degradation of the polymer in the presence of pro-oxidant was found to follow the order: 20BPE greater than 10BPE greater than PE. The oxo-biodegradable additive added PE offers a much better alternative to traditional PE—based products.

Hence the PE with oxo-biodegradable additive containing pro-oxidant can be used in packaging industry and will be helpful in controlling the plastic litter management.

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## References

1. Moura EAB, Ortiz AZ, Wiebeck H, Paula ABA, Silva ALA, Silva LGA (2004) Effects of gamma radiation on commercial food packaging films—study of changes in UV/VIS spectra. *Radiat Phys Chem* 71:199–202
2. Ojeda TFM, Dalmolin E, Forte MMC, Jacques RJS, Bento FM, Camargo FAO (2009) Abiotic and biotic degradation of oxo-biodegradable polyethylenes. *Polym Degrad Stab*. doi:10.1016/j.polymdegradstab.03.011
3. Scott G (2000) “Green” polymers. *Polym Degrad Stab* 68:1–7
4. The Times of India (2009) Vol 2: Issue 197, p.2
5. Khabbaz F, Albertsson AC (2001) Rapid test methods for analyzing degradable polyolefins with a prooxidant system. *J Appl Polym Sci* 79:2309–2316
6. Otey FH, Westhoff RP, Dane WM (1987) *Ind Eng Chem Res* 26:1659
7. Kemp TJ, McIntyre RA (2006) Influence of transition metal-doped titanium (IV) dioxide on the photodegradation of polyethylene. *Polym Degrad Stab* 91:3020–3025
8. Roy PK, Surekha P, Rajagopal C, Choudhary V (2006) Effect of cobalt carboxylates on the photo-oxidative degradation of low density polyethylene. Part –I. *Polym Degrad Stab* 91:1980–1988
9. Shah PB, Bandopadhyay S, Bellare JR (1995) Environmentally degradable starch filled low density polyethylene. *Polym Degrad Stab* 47:165–173
10. Pometto III AL, Lee B, Johnson KE (1992) Production of an extracellular polyethylene-degrading enzyme(s) by *Streptomyces* species. *Appl Environ Microbiol* 61:731–733
11. Wiles DM, Scott G (2006) Polyolefins with controlled environmental degradability. *Polym Degrad Stab* 91:1581–1592
12. Roy PK, Surekha P, Raman R, Rajagopal C (2009) Investigation the role of metal oxidation state on the degradation behaviour of LDPE. *Polym Degrad Stab* 94:1033–1039
13. Gorghiu ML, Jipa S, Zaharescu T, Setnescu R, Mihalcea I (2004) The effect of metals on thermal degradation of polyethylenes. *Polym Degrad Stab* 84:7–11
14. Magagula B, Nhlapo N, Focke WW (2009)  $Mn_2Al$ -LDH- and  $Co_2Al$ -LDH-stearate as photodegradants for LDPE film. *Polym Degrad Stab* 94:947–954
15. Corti A, Muniyasamy S, Vitali M, Imame SH, Chiellini E (2010) Oxidation and biodegradation of polyethylene films containing pro-oxidant additives: Synergistic effects of sunlight exposure, thermal aging and fungal biodegradation. *Polym Degrad Stab* 95:1106–1114

16. Lee B, Pometto AL III, Fratzke A, Bailey TB (1991) Biodegradation of degradable plastic polyethylene by *Phanerochaete* and *Streptomyces* species. *Appl Environ Microbiol* 57:678–685
17. Khabbaz F, Albertsson A-C, Karlsson S (1999) Chemical and morphological changes of environmentally degradable poly(ethylene) films exposed to thermo-oxidation. *Polym Degrad Stab* 63:127–138
18. Jakubowicz I (2003) Evaluation of degradability of biodegradable polyethylene (PE). *Polym Degrad Stab* 80:39–43
19. Gugumus F (2001) Re-examination of the thermal oxidation reactions of polymers. New views of an old reaction. *Polym Degrad Stab* 74:327–339
20. Sudhakar M, Trishul A, Doble M, Suresh Kumar K, Syed Jahan S, Inbakandan D, Viduthalai RR, Umadevi VR, Sriyutha Murthy P, Venkatesan R (2007) Biofouling and biodegradation of polyolefins in ocean waters. *Polym Degrad Stab* 92:1743–1752
21. Navaneetha Pandiyaraj K, Selvarajan V, Deshmukh RR, Gao C (2008) Adhesive properties of polypropylene (PP) and polyethylene terephthalate (PET) film surfaces treated by DC glow discharge plasma. *Vacuum* 83:332–339
22. Roy PK, Titus S, Surekha P, Tulsi E, Deshmukh C, Rajagopal C (2008) Degradation of abiotically aged LDPE films containing pro-oxidant by bacterial consortium. *Polym Degrad Stab* 93:1917–1922
23. Baljit Singh and Nisha Sharma (2008) Mechanical implications of plastic degradation. *Polym Degrad Stab* 93:561–584
24. Kaczmarek H, Oldak D, Podgorski A (2003) Photochemical properties of polyethylene modified by low-molecular organic compounds. *Polym J* 35(8):634–639
25. JWT Spinks, RJ Woods (1990) *Int Rad Chem* 3 Edn. Wiley, N Y, p. 468
26. Bikaris D, Prinos J, Perrier C, Panayiotou C (1997) Thermo analytical study on the effect of EAA and starch on the thermooxidative degradation of LDPE. *Polym Degrad Stab* 57:313–324
27. Wenzel RN (1936) Resistance of solid surfaces to wetting by water. *Ind Eng Chem* 28:988
28. Jose S, Thamas S, Biju PK, Koshy P, Karger-Kocsis J (2008) Thermal degradation and crystallisation studies of reactively compatibilised polymer blends. *Polym Degrad Stab* 93:1176–1187