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Thermal stability and degradation of the post-use reclaim milk pouches during multiple extrusion cycles

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Abstract

In the present study, the recyclability of the post-use milk pouches (50/50 LDPE–LLDPE blend) was evaluated with or without adding stabilizer. Thoroughly washed and dried post-use milk pouch films were extruded five times at high temperature (483–513 K) in the open atmosphere. The mode of degradation during extrusion operation was studied by melt flow index (MFI), rheological properties, gel content and FT-IR analysis. The differential scanning calorimetry (DSC) analysis was carried out to evaluate the thermal stability of the stabilized and un-stabilized recycled mass from post-use milk pouch under this investigation. Mechanical properties (tensile strength, % elongation at break, tensile modulus and hardness) of the un-stabilized extruded material were significantly affected as a result of thermooxidative degradation during extrusion in presence of air. After all, stabilization with 0.4% anti-oxidant satisfactorily retains all the initial properties of the recycled material.

Keywords: Recycling; Polyethylene; Degradation; Stabilization; Post-use milk pouches

1. Introduction

In India, a huge quantity of polyethylene raw materials, particularly low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) are consumed in the packaging of the liquid milk (46% of the total milk product), because the distribution outlet of this milk in the domestic sector is exclusively achieved through polyethylene packaging. Report shows that about 33,000 metric t of polyethylene was consumed in India in the year 1995 and the figure increased to 40,000 metric t in 1997 [1,2]. Therefore, the effort to reduce, reuse and recycle of these post-use packaging films has become a challenging task to avoid adverse environmental impact as well as to restrict the raw material consumption.

Several popular methods such as mechanical recycling, chemical or feedstock recycling, energy recovery or incineration, etc. are used to reclaim or recycle the plastic waste materials. But, the mechanical recycling is the most preferable method to most of the recycling industries both in developed and under developed countries due to its technical and economical feasibility. So far as the mechanical recycling of the plastic wastes is concerned, the collected and segregated materials are generally reprocessed through melt extrusion at high temperature and at high extrusion speed in the atmospheric condition. As the inherent properties of polymer materials, particularly polyethylene, are adversely affected by temperature, shear and oxygen [3], they could easily undergo numerous thermooxidative and thermomechanical degradations during the reprocessing treatment. That causes irreversible changes in the structure and physical properties of the polymer, which deteriorate the quality of the end products [4–7].

However, the thermooxidative and thermomechanical degradations of polyethylene are initiated with the formation of reactive free radicals (macro radical), which then

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propagate though chain scission and crosslinking reactions competitively and simultaneously depending upon the processing conditions (temperature, shearing rate and atmosphere), molecular structure of the polymer and the type of catalyst used during manufacturing of the polymer [7,8]. It was well studied that for Phillips-type high-density polyethylene, the crosslinking reaction predominates over the chain scission during the melt reprocessing. But for Ziegler-type high-density polyethylene and polypropylene the situation is reverse, i.e., the chain scission is the dominating mechanism of degradation [9–12]. Holmström et al. [13] found that both the chain scission and molecular enlargement reactions occur on thermal degradation of the LDPE in nitrogen atmosphere having less than 0.0005% oxygen. However, these two degradation mechanisms have opposite effects on the molecular weight and molecular weight distribution of the polymer. The molecular weight decreases with increasing chain scission reaction whereas the same increases with increasing crosslinking reaction. This is reflected through the facts that the physical characteristics, e.g., melt flow index (MFI), tensile strength, percent elongation at break, hardness, impact strength, percent crystallinity, melting temperature, etc. of the recycled polymer do not exactly match with that of the virgin raw polymer.

In this context, it must be mentioned that after the first service life the residual stabilizer would not at all be sufficient to provide necessary stability to the recycled polymer for second term application. Many authors have reported that the stability of the recycled polymer could be successfully improved by the addition of optimum quantity of stabilizer [8,11,12,14–16]. Drake [17] and Drake et al. [18] have used Irganox 1010, Irgafos 168 as processing stabilizer in order to improve the quality of recycled materials obtained from HDPE bottle crates and got successful results. Herbst et al. have reported that the Recyclostab^{TM} 411 at the level of 0.2 wt.% can maintain constant MFI of the recycled HDPE even over five extrusion passes at 523 K [19].

The use of the recycled LDPE–LLDPE blend is enormously increasing in our practical life. The most selective applications of this recycled material are commodity products such as refuge sacks, carrier bags, agriculture films, heavy-duty sacks, household products etc. Therefore, the proper recycling of these waste milk pouches could open up a new application sector.

In this paper, a comparative study on variation of the properties of both un-stabilized and stabilized recycled polymers recovered from post-use milk pouches as a function of multiple extrusions has been made. The aim of this work is to investigate the viability of the recycled material in second life application with or without stabilization.

2. Experimental

2.1. Materials

The raw material used in this work is thoroughly washed and dried post-use milk pouches (MFI = 0.758 g/10 min at 463 K with 2.16 kg load) collected from the municipal garbage, Ranchi City, India. The co-extruded multi-layered milk pouches were manufactured for milk packaging using a 50/50 blend of low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) obtained from Indian Petrochemical Corporation Ltd. (IPCL). The specification details of the polymers (i.e. LDPE and LLDPE) used in the manufacture (Manufacturer: Bihar State Co-operative Milk Producers Federation Ltd., India) of these milk pouches are given in Table 1. The detergent and NaOH used for washing of these waste pouches were obtained from Nirma Ltd., India and E. Merck India Ltd., respectively.

The anti-oxidant, Irganox B 225 was collected from Ciba Specialty Chemicals (India) Ltd. The Irganox B 225 is a 1:1 blend of Irganox 1010 ($M_w = 1178$, $T_m = 383–398$ K) and Irgafos 168 ($M_w = 647$, $T_m = 453–459$ K).

2.2. Methods

At the initial stage of this work, the collected milk pouch films were washed with aqueous solution of 3% NaOH and 12% detergent under boiling condition for 30 min to clean adhered fats/fatty acids and then dried in an air oven at 313 K for 48 h.

The extrusion of the dried films was made with the HAAKE (Rheocord 9000) single-screw extruder attached with Rheomex-254 in open atmosphere. Experimental conditions followed for this operation are presented in Table 2. Two batches of the materials were prepared, one containing 0.4% (w/w) anti-oxidant (Irganox B 225) and another was without antioxidant. For each of the aforementioned batches, five consecutive extrusion cycles were performed. Hence each

Table 1
Polymers and their specifications used in the manufacturing of milk pouches

Polymer	Grade	Co-monomer	MFI[a] (g/10 min)	Density (kg/m^3)	Tensile strength (MD[b]/TD[c]) (MPa)	Percentage of elongation at break (MD[b])
LDPE	1005FY20	–	0.4–0.7	$0.921–0.923 \times 10^3$	21.1/19.6	300–500
LLDPE	LL20FS010	Octene	1.0	$0.918–0.920 \times 10^3$	39.2/29.4	700–800

[a] Melt flow index at 463 K and load 2.16 kg.
[b] Machine direction.
[c] Transverse direction.

Table 2
Conditions used in single screw extrusion and screw injection molding process

Process	Temperature (K)					Screw speed (rpm)
Extrusion	483 (zone 1)	493 (zone 2)	503 (zone 3)	513 (zone 4)	293–298 (water bath)	60
Injection molding	483 (zone 1)	493 (zone 2)	503 (zone 3)	513 (die)	293–298 (mold)	60

batch contained five sets of samples from five multiple extrusion cycles. The average residence time of each extrusion cycle was 63 s. After each extrusion operation, the extruded profiles were cooled by passing through water bath at room temperature followed by chopping and drying in an air oven at 323 K for 1 h.

The films used for infrared (IR) spectroscopic analysis were prepared in compression molding machine (Precision System and Innovations (PSI) Sales Pvt. Ltd., India, Model No. 9925) at 423 K.

The specimens for tensile test (ASTM D638, type-I) were prepared in DGP Windsor Injection Molding Machine (model ST-25). Processing conditions for extrusion and injection molding are presented in Table 2.

2.3. Characterization

The melt flow index (MFI) was measured using DAVENPORT melt flow indexer (Serial No. 3/2225). The experiment was carried out under the conditions mentioned in ASTM D1238 method (cylinder temperature 463 K and 2.16 kg load). The average of five consecutive results was taken for each sample.

The rheological properties of each sample were measured at 493 K in the HAAKE Rotovisco (RT-20) cone and plate (0.035 m diameter) rheometer using 2° angle. The oscillating frequency ranged from 10^{-2} to 10^{2} rad/s was considered for each measurement.

The percent gel content was directly evaluated by extracting the soluble fraction with hot xylene solution followed by hot filtration. The weight of the gel fraction (filtered part) was taken after vacuum drying.

Infrared spectra (Attenuated Total Reflectance, ATR) of the compression-molded films were obtained by FT-IR Thermo Nicolet (NEXUS 870) spectrophotometer at room temperature (303 K).

Differential scanning calorimetry (DSC) analysis was carried out in the METTLER DSC 25 attached with METTLER TC114000 thermal analyzer. For each formulated sample, two heating scans (from 303 to 773 K), one in nitrogen atmosphere and another in air atmosphere were executed. Each scan was carried out at the heating rate of 10 K/min.

Tensile properties of each of the reprocessed material were determined by HOUNSFIELD (Model H10KS) tensile testing machine, using crosshead speed 0.05 m/min at room temperature (303 K).

The hardness of the samples were measured according to ASTM D2240 standard method at room temperature (303 K) and expressed in shore D.

3. Results and discussion

MFI of the un-stabilized recycled material (LDPE–LLDPE blend), shown as a function of number of reprocessing cycles in Fig. 1, initially decreases with increasing number of extrusion cycles (from first to third cycle) followed by gradual increase to fifth cycle. The reason for initial decrease of MFI for un-stabilized recycled material may be attributed to predominant crosslinking over chain scission. But, after stabilization with antioxidant, it is found that the MFI shows an increasing trend, although small, from first to fifth extrusion cycles. This observation is an indication of molecular weight decrease of the polymer by chain scission only in presence of antioxidant. Antioxidant prevents crosslinking by coupling with fragmented polymer radicals.

The flow curves of the un-stabilized and stabilized recycled milk pouches are shown in Fig. 2. Other than viscosity decrease no distinctive feature is visible from the flow curves with increase in shear frequency in all extrusion cycles. The curves show that the viscosity of the un-stabilized recycled polymer decreases more rapidly than that of the stabilized polymer at higher frequency (shear rate) region. It indicates that the melt strength of the un-stabilized recycled LDPE–LLDPE blend is inferior to that of the stabilized one. The zero-shear viscosity of each sample under this investigation corresponds to their complex viscosity values at $\omega = 0.012$ rad/s [20]. It is well observed for both the un-stabilized and stabilized recycled milk pouches (LDPE–LLDPE blends) that the zero shear viscosity (Fig. 3) and MFI values (Fig. 1) change in a reverse manner as a function of number of extrusion cycles.

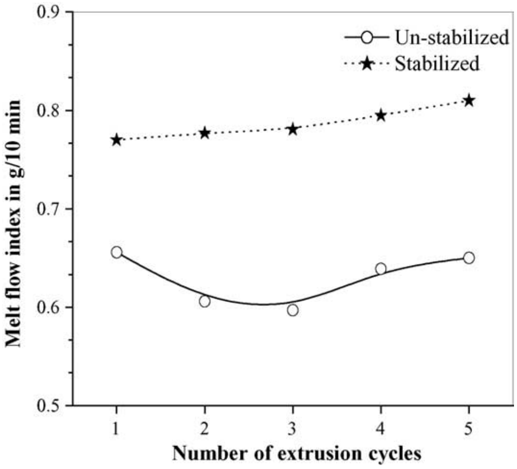

Fig. 1. Variation of MFI (at 463 K) as a function of number of extrusion cycles for the un-stabilized and stabilized recycled milk pouches.

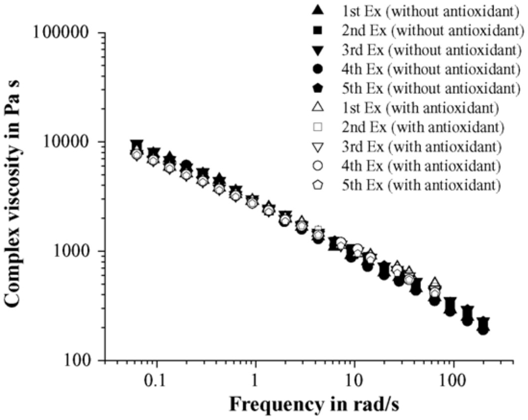

Fig. 2. Flow curves of the un-stabilized (filled symbols) and stabilized (unfilled symbols) recycled milk pouches at 493 K.

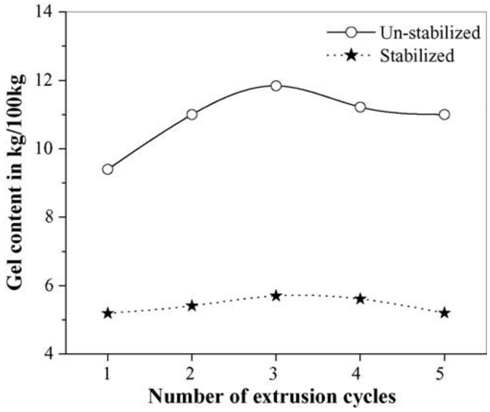

Fig. 4. Variation of gel content as function of number of extrusion cycles for the un-stabilized and stabilized recycled milk pouches.

The results shown above, i.e., the decrease in MFI and the increase in zero shear viscosity from the beginning of the reprocessing cycles (i.e. from first to third extrusion cycle) indicates that thermomechanical degradation of the un-stabilized recycled material (LDPE–LLDPE blend) is initiated with simultaneous crosslinking reactions leading to the enhancement of molecular weight of the polymer [10]. Chakraborty and Scott [3] have also reported identical finding, i.e., decrease in MFI from the beginning of processing of low-density polyethylene (LDPE) in low oxygen atmosphere at 423 K and suggested rapid crosslinking. On the other hand, the increase in MFI values and the decrease in zero shear viscosity at subsequent fourth to fifth extrusion cycles could be attributed to an extensive shearing force at high temperature in presence of atmospheric oxygen, which may lead to intensify the thermomechanical chain scission.

The increase of gel content as a function of processing cycles, illustrated in Fig. 4, again shows a dominating tendency of the un-stabilized recycled LDPE–LLDPE blend to form crosslink in the first three extrusion cycles [3], whereas the chain scission reaction is found to be dominated in the last two cycles (fourth and fifth cycle). However, the addition of 0.4% anti-oxidant to the recycled material before extrusion has reduced the gel content throughout the whole range of processing cycles (Fig. 4).

From the IR spectroscopic analysis, the wavelength regions chosen for evaluation of the thermooxidative degradation of the un-stabilized recycled polymer are 3800–3200, 1800–1650 and 1000–870 cm^{-1}.

The free hydroperoxides and hydroxyl groups generated as a result of oxidation of the un-stabilized recycled LDPE–LLDPE blend during reprocessing were well identified by IR spectroscopy and are shown in Fig. 5. The bands at 3594 cm^{-1} (–OOH) and 3370 cm^{-1} (–OH) are attributed to the free hydroperoxides and hydroxyl groups, respectively. Rugg et al. [21] also found identical IR-bands at $\sim$3557 cm^{-1} for hydroperoxides and $\sim$3367 cm^{-1} for hydroxyl groups in melt oxidized polyethylene sample. Interestingly, it was also observed that the concentration of hydroperoxide, hydroxyl, and ester carbonyl and vinyl groups changed with increasing the number of extrusion cycles. In Fig. 6, it is observed that the absorbance of the –OOH band from the beginning of the extrusion cycles is gradually decreased to a minimum at third extrusion cycle followed by sharp increase at fourth

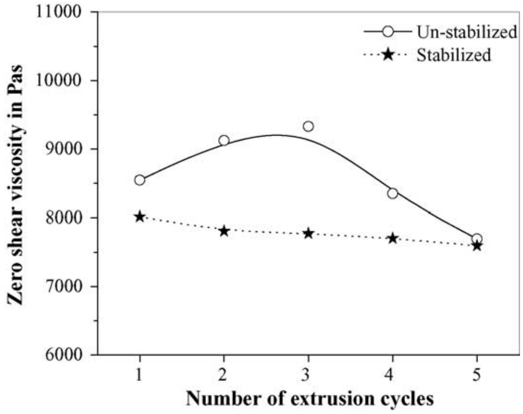

Fig. 3. Variation of zero shear viscosity as function of number of extrusion cycles for the un-stabilized and stabilized recycled milk pouches at 493 K.

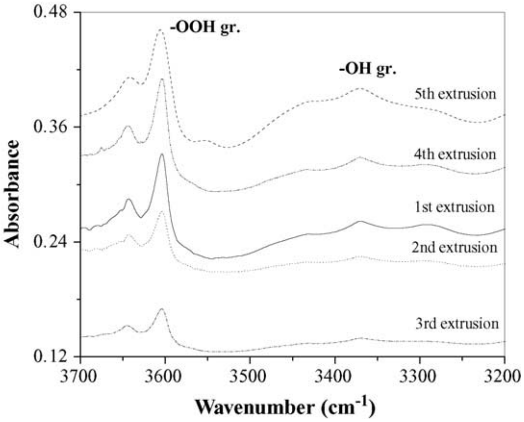

Fig. 5. The –OOH and –OH stretching region of the multi-extruded un-stabilized recycled milk pouches.

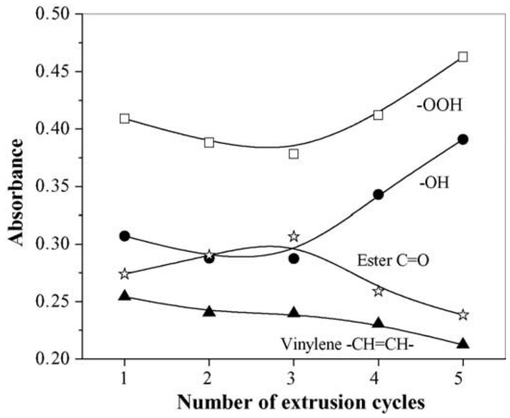

Fig. 6. Change of absorbance of hydroperoxide, hydroxyl and vinylene groups as a function of number of extrusion cycles for un-stabilized milk pouches.

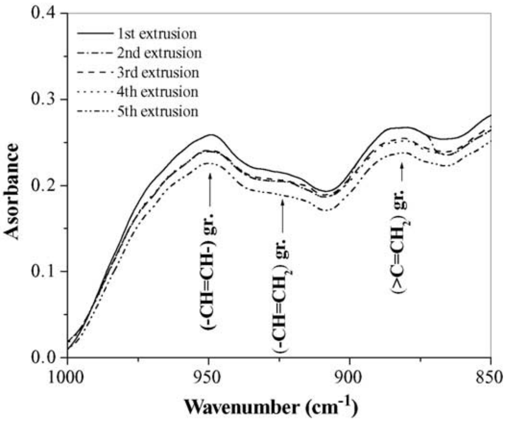

Fig. 8. IR-bands of unsaturated aliphatic groups for the multi-extruded un-stabilized recycled milk pouches.

and fifth extrusion cycles. The low peroxide concentration at the initial stage of extrusion cycles is due to the low oxygen content in the reaction medium, and the alkyl free radicals formed from the initial fragmentation of the macromolecules show a greater tendency to undergo recombination reaction, i.e., molecular rearrangement [3,22,23] instead to react with oxygen free radicals to form peroxides.

The carbonyl groups developed by the thermooxidative degradation of the un-stabilized LDPE–LLDPE blend are observed in the IR-region of 1800–1600 cm^{-1} presented in Fig. 7. The bands observed at 1748, 1727, 1714 and 1682 cm^{-1} are attributed to the carbonyl (C=O) stretching vibrations of the ester (–COOR), aldehyde (–CHO), ketone (>C=O) and α,β-unsaturated ketone groups, respectively [24–26]. In Fig. 7, it is seen that the area of the ester carbonyl band gradually increased from first to third cycle whereas no such C=O band is found for materials obtained in the fourth and fifth cycles, which is well reflected on the corresponding absorbance values (Fig. 6). Holmström and Sörvik [27] studied structural changes in both LDPE and HDPE during thermooxidative degradation and presented a degradation mechanism where they have shown formation of ester, aldehyde and ketonic groups. In our study of multiple extrusions with recycled LDPE–LLDPE blend we also observed a gradual increase of absorbance of the ester carbonyl band in the first three cycles. Such increase in absorbance value of ester carbonyl group is clearly due to molecular enlargement reaction occurred during series of thermooxidative reactions in presence of air [27–29], besides the combination of the alkyl free radicals. Surprisingly the ester carbonyl band gradually disappeared in the subsequent fourth and fifth extrusion cycles, the reason for which is not clear to us. One possibility, which still remains to be explored, may be decarboxylation on repeated thermal exposure in fourth and fifth extrusion cycles.

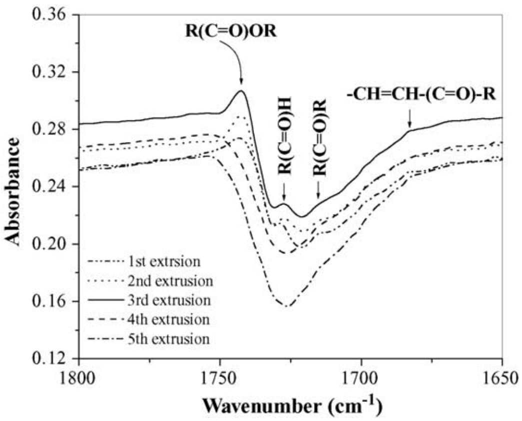

Fig. 7. Carbonyl stretching region of the multi-extruded un-stabilized recycled milk pouches.

The olefinic unsaturated groups appeared as a result of degradation of the un-stabilized recycled polyethylene are also well identified in the IR-region of 1000–870 cm^{-1}, shown in Fig. 8. The bands observed at ∼950, ∼912 and ∼888 cm^{-1} correspond to the vibrations of vinylene (–CH=CH–), vinyl (–CH=CH_2) and vinylidene (>C=CH_2) groups, respectively. The absorbance of the vinylene group, which reflects its corresponding concentration in the sample is recorded to be maximum value at the first cycle and exhibited minimum value at the fifth cycle (Fig. 6). The higher concentration of olefinic unsaturation in the un-stabilized recycled material is considered to be a good approximation of its susceptibility to crosslinking reaction [30].

The influence of thermomechanical treatment during multiple extrusions of recycled milk pouch polymers (LDPE–LLDPE blend) on their thermal stability was assessed by DSC analysis. The transition temperatures of all samples and their degradation enthalpy values evaluated by DSC analysis in N_2 atmosphere are shown in Table 3 and those in air atmosphere are shown in Table 4. The thermal stability of the recycled material even without stabilization is found to be expectedly higher in the N_2 atmosphere as compared to that in air atmosphere. In the DSC heating scan in N_2 atmosphere, two melting peaks (∼384 and ∼399 K) are found for both un-stabilized and stabilized recycled LDPE–LLDPE

Table 3
DSC analysis during first heating scans in nitrogen atmosphere for un-stabilized and stabilized recycled milk pouches after multiple extrusion cycles

Number of extrusion cycles	Un-stabilized material					Stabilized material				
	T_m[a] (K)		T_d[b] (K)	ΔH_d[c] (kJ/kg)	X_{cr}[d] (%)	T_m[a] (K)		T_d[b] (K)	ΔH_d[c] (kJ/kg)	X_{cr}[d] (%)
	Peak I	Peak II				Peak I	Peak II			
First	384	399	775	504	41.5	385	399	782	466	44.7
Second	384	398	722	504	37.8	385	398	784	427	41.7
Third	383	399	705	501	36.0	384	397	780	411	41.3
Fourth	384	398	741	507	33.8	384	399	779	460	40.7
Fifth	384	397	750	504	33.1	385	398	780	465	39.8

[a] Crystalline melting temperature.
[b] Degradation temperature.
[c] Enthalpy of degradation endotherm.
[d] Percent crystallinity.

samples. The theoretical T_m for LDPE is ~384 K and that for LLDPE is ~397 K. This observation indicates that even after multiple extrusions crystalline phases of both LDPE and LLDPE in the blend remain separated, because LDPE and LLDPE are practically immiscible in crystalline phase [31]. Similar observation was also obtained for both the un-stabilized and stabilized recycled materials when the DSC analysis was run in air atmosphere. The percent crystallinity (X_{cr}) of both the un-stabilized and stabilized recycled polymers is found to decrease with increasing the number of extrusion cycles as presented in Tables 3 and 4. The lowering of crystallinity could be attributed to the creation of structural irregularity by formation of short branches in the backbone chain and groups, e.g. hydroxide, hydroperoxide, carbonyl, aliphatic vinyl, etc. which reduce the close packing ability of the polymer chains, and hence decrease the polymer crystallinity [27]. However, the degree of crystallinity of the recycled LDPE–LLDPE blend was improved by stabilization with antioxidant. An exothermic peak occurred for all samples due to thermooxidative degradation of the polymer when the DSC analysis was run in air, in which both the onset and peak temperatures of the oxidation exotherm are found to be remarkably higher in case of the stabilized recycled material in comparison to un-stabilized material (Table 4). The above results indicated that the thermal stability of the recycled polymer could be significantly improved by proper stabilization.

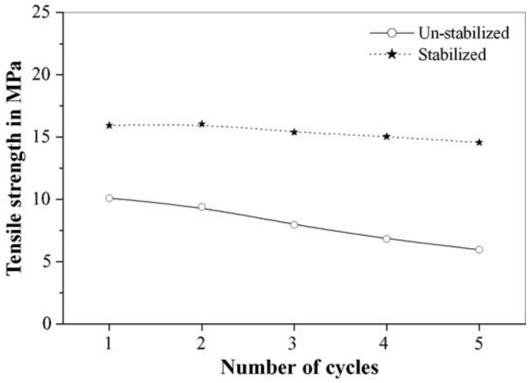

Fig. 9. Effect of multiple extrusions on the tensile strength of un-stabilized and stabilized recycled milk pouches.

The variation of tensile strength, percent elongation at break, tensile modulus and hardness as a function of number of extrusion cycles is demonstrated in Figs. 9–12. Although both stabilized and un-stabilized polymers showed gradual decrease of tensile strength with increasing number of extru-

Table 4
DSC analysis during first heating scans in air atmosphere for un-stabilized and stabilized recycled milk pouches after multiple extrusion cycles

Number of extrusion cycles	Un-stabilized material						Stabilized material					
	T_m[a] (K)		T_{ox}[b] (K)		ΔH_{ox}[c] (kJ/kg)	X_{cr}[d] (%)	T_m[a] (K)		T_{ox}[b] (K)		ΔH_{ox}[c] (kJ/kg)	X_{cr}[d] (%)
	Peak I	Peak II	Start	Peak			Peak I	Peak II	Start	Peak		
First	385	399	483	510	347	36	385	399	527	542	282	41
Second	385	398	473	506	450	35	385	398	527	535	275	42
Third	385	398	473	506	418	33	385	398	527	538	315	39
Fourth	384	399	463	505	380	32	385	398	527	535	304	34
Fifth	384	399	468	504	331	30	384	398	523	534	353	36

[a] Crystalline melting temperature.
[b] Oxidative degradation temperature.
[c] Enthalpy of oxidation exotherm.
[d] Percent crystallinity.

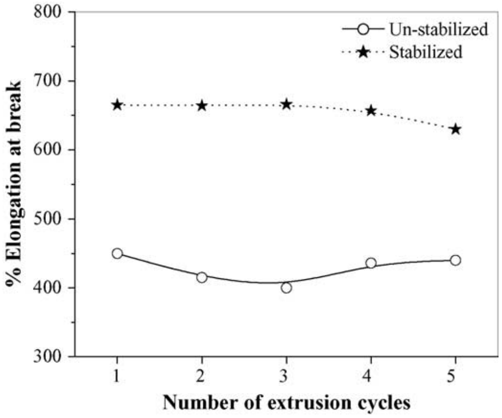

Fig. 10. Effect of multiple extrusions on the elongation at break of un-stabilized and stabilized recycled milk pouches.

sion cycles, the decrease is more pronounced for un-stabilized material (Fig. 9), whereas for the un-stabilized material the percent elongation at break exhibited a decreasing trend from first cycle to third cycle followed by increasing through fourth to fifth cycle (Fig. 10). The decrease in percent elongation at break at the initial stage of extrusion cycles (first to third) is due to the crosslinking reaction [32] whereas, the subsequent enhancement (in fourth to fifth extrusion cycles) may be due to an extensive chain scission reaction developing free volume between polymer chains that allowing the chains to move freely. However, stabilization of the recycled LDPE–LLDPE blend with antioxidant exhibits improvement in both their tensile strength and percent elongation at break (extensibility) (Figs. 9 and 10). The tensile modulus, presented in Fig. 11, of the un-stabilized recycled LDPE–LLDPE blend changes in reverse manner to that followed in the case of percent elongation at break with increasing the number of processing cycles, i.e., initially rises up to third extrusion step followed by reduction in the last two cycles (fourth and fifth). This observation indicates that during the initial stage of reprocessing operation the material becomes stiffer and harder in nature, which may be due to crosslinking effect [10,33] causing the polymer chains pulling closer, leaving less free volume that restricts their mobility [34] and hence produces more stiff and harder material. The change of hardness of the recycled polymer as function of number of reprocessing cycles is presented in Fig. 12. Although the hardness of the unstabilized polymer increased up to third extrusion and then decreased in subsequent extrusions but the same for the stabilized polymer remained almost constant up to fourth extrusion cycle and then increased in fifth cycle.

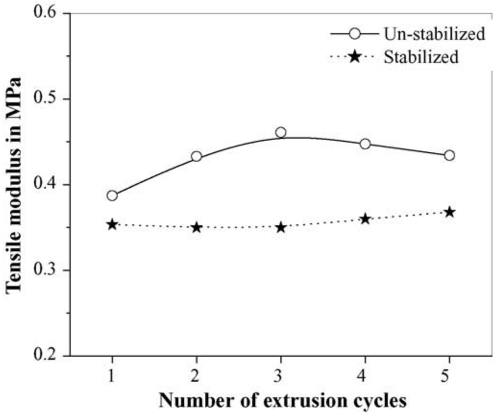

Fig. 11. Effect of multiple extrusions on the tensile modulus of un-stabilized and stabilized recycled milk pouches.

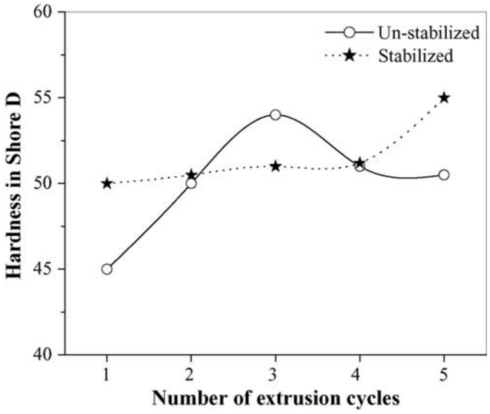

Fig. 12. Effect of multiple extrusions on the hardness of un-stabilized and stabilized recycled materials.

4. Conclusion

The recyclability of the post-use milk pouches containing 50/50 LDPE–LLDPE blend was explored and their thermal and mechanical properties were evaluated. Since the post-use milk pouches are supposed to be subjected to reprocessing operation, thoroughly washed and dried post-use milk pouch films were extruded five times at 483–513 K in air. Although the mechanical properties of the un-stabilized extruded material were significantly affected as a result of thermooxidative degradation during multiple extrusions in presence of air but addition of 0.4% anti-oxidant satisfactorily retained all the initial properties of the recycled milk pouch polymers. This investigation has enabled us to know the variation of MFI, zero shear viscosity, gel content of the recycled polymer from milk pouch as a function of number of extrusion cycles and from FT-IR spectroscopic analysis some idea of chemical changes occurred during such multiple extrusions due to thermooxidative degradation. The results of this investigation may help solution of waste disposal problem.

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