Aluminium-Filled Low-Density Polyethylene—Structural, Morphological, and Mechanical Properties

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ABSTRACT: Low-density polyethylene (LDPE) was filled with aluminium (Al) powder having concentrations of 1, 4, and 6% w/w. The samples in the form of disc containing the above concentration of Al powder were obtained using hot press molder. The structural properties have been investigated using density measurement and WAXD techniques. The morphology of pure LDPE and Al-filled LDPE samples has been studied from scanning electron micrographs. The modulus of elasticity of the samples has been determined using Instron tensile tester. Results indicate that the crystallinity of LDPE component increases with the concentration of aluminium filler. Morphological changes also have been observed. The Young's modulus (*Y*) generally increases and becomes maximum for 4% Al-filled LDPE sample. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2436–2441, 2007

Key words: LDPE; filler; aluminium; structural; mechanical

INTRODUCTION

Low-density polyethylene (LDPE) is a commercially popular material being corrosion-free and having low cost. One of the primary reasons for semicrystalline polymer like LDPE to be important is its good mechanical properties.

The effect on structural, mechanical, and morphological properties of polymers due to addition of various fillers has been the subject of many studies.[1–4] In the last 30 years, a lot of work has been carried out to study improvement in structural and mechanical properties in polyethylene, specially LDPE.[5,6]

From literature survey, it has been found that most of the reports are concerned about the properties of polymers where fillers used are of very high concentration (10–50% w/w).[7] Hence, it was thought appropriate to study structural, morphological, and mechanical properties of Aluminium (Al)-filled LDPE, where percentage by weight of filler is deliberately kept low (1–6% w/w) so that the cost of the composite is reduced.

The second purpose of carrying out this type of work is to prepare low-cost material with improved structural as well as mechanical properties by addition of low concentration of filler so that composite can be used in various applications.

It is well known that conductor-filled polymers are of greater interest as they show drastic increase in physical properties.[8] In the present work, aluminium powder having a concentration of 0.5, 1, 4, and 6% w/w is used as a filler in LDPE matrix and the structural, morphological, and mechanical properties have been reported.

SAMPLE PREPARATION

The samples in the form of a disc have been prepared using a hot-press molder (Fig. 1). The samples of pure LDPE, 1% Al powder-filled LDPE, 4% Al powder-filled LDPE, and 6% Al powder-filled LDPE have been prepared in the form of a disc having a thickness of 0.1 cm and a diameter of 5 cm.

For preparation of disc, commercially available granuals of LDPE and given concentrations of Al filler have been mixed (eg. for preparation of 1% Al-filled LDPE, 1 g of Al powder is mixed with 100 g of LDPE). This physical mixture is used in simple hot-press molder to obtain a disc.

EXPERIMENTAL TECHNIQUES

Density measurement

Density of samples have been measured using Moore and Sheldon's floatation technique.[9] For measurement of density of pure LDPE and Al-filled LDPE, a mixture of benzene (AR grade) having a density of 0.87 g/cm^3 and carbon tetrachloride having a density of 1.59 g/cm^3 have been used.

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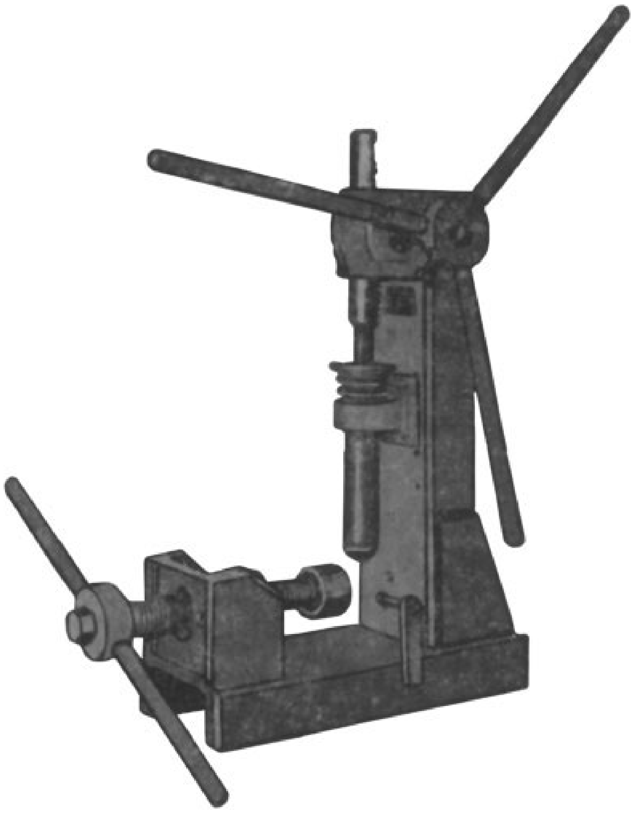

Figure 1 Hot press molder.

WAXD pattern

The WAXD patterns have been recorded using Philips X-ray generator PW 1929 and automatic X-ray diffractometer model PW 1729 unit. WAXD patterns have been scanned at the rate of 2.4°/min in reflection mode over range of 2θ from 0 to 40°.

From radial scan of intensity versus 2θ, the lateral order or crystallinity index was determined using Manjunath's formula[10] which is given as

$$R = \frac{m_1 + 2m_2 + \cdots + m_{n-1}}{h_1 + h_2 + \cdots + h_n}$$

where m_1, m_2 is the heights of minimum between two peaks and h_1, h_2 is the heights of the peaks from the base line.

The crystallite size was determined by Scherrer's formula[11] which is given as

$$D_{hkl} = k\lambda/\beta \cos\theta$$

where D_{hkl} is the crystallite size in a diffraction perpendicular to plane (h,k,l) corresponding to measured reflection.

λ is the wave length of radiation used (1.542 Å)
k is the constant (0.9 for polymers)
β is the half maximum width in radians
θ is the Bragg's angle

Scanning electron microscopy

The morphology of samples has been investigated using JXA 840A scanning electron microscope. The microscope was normally operated in secondary emission mode at 20 kV.

Initially large area of sample has been observed at a low magnification and then the required areas have been examined at higher magnification.

Mechanical properties

Mechanical properties [% strain at break, load at break, and Young's modulus (Y)] have been measured using Instron tensile tester. The sample of thickness 0.1 cm, length 5 cm, and width 1 cm was gripped between two jaws such that specimen length was about 2.5 cm. The cross-head speed was maintained at 50 mm/min.

RESULTS AND DISCUSSION

Structure of Al-filled LDPE

Structural investigations of pure LDPE and Al-filled LDPE have been carried out by two methods

i. Density measurements
ii. WAXD Techniques

Densities of Al powder-filled LDPE composites

Table I gives theoretically calculated and experimentally obtained values of pure and Al-filled LDPE composites. Theoretical values are obtained by using simple expression of density = mass/volume. These values are calculated by using density of pure LDPE and assuming that Al-filled LDPE samples are made up of two components—LDPE and Al.

Without addition of filler the density of pure LDPE sample is 0.922 g/cm^3 and is slightly more than the reported value of density, which is 0.920 g/cm^3. However, for 1% Al-filled, 4% Al–filled, and 6% Al-filled samples the experimentally obtained values are found to be less than theoretically calculated values of respective samples.

TABLE I
Theoretical and Experimental Values of Density

Concentration of filler (%)	Theoretically calculated values of density (g/cm^3)	Experimentally obtained values (g/cm^3)
0	0.920	0.922
1	0.928	0.926
4	0.946	0.935
6	0.958	0.954

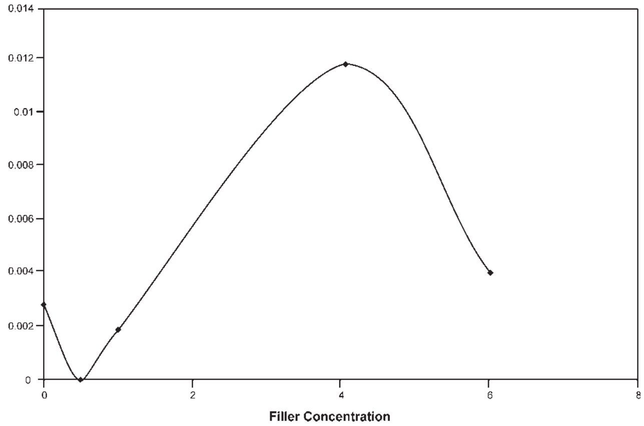

Figure 2 Graph of density difference versus filler concentration.

The difference in experimentally obtained and theoretically calculated values is because of the reduction in the values of density of LDPE component in respective samples, as the density of aluminium will not change.

It is clear that the density of aluminium does not change, but density of LDPE can vary with the change in crystallinity. Thus the smaller values of density for the filled samples show that the crystallinity of LDPE component is changing. The reason for decrease in density is associated with decrease in crystallinity. However, X-ray results show that there is marginal increase in crystallinity of filled samples. Hence, reason for decrease in density is because of the presence of voids formed during sample preparation. To ascertain the morphologies of all pure and filled LDPE, samples have been studied using SEM at two magnifications, which show presence of voids during sample preparation.

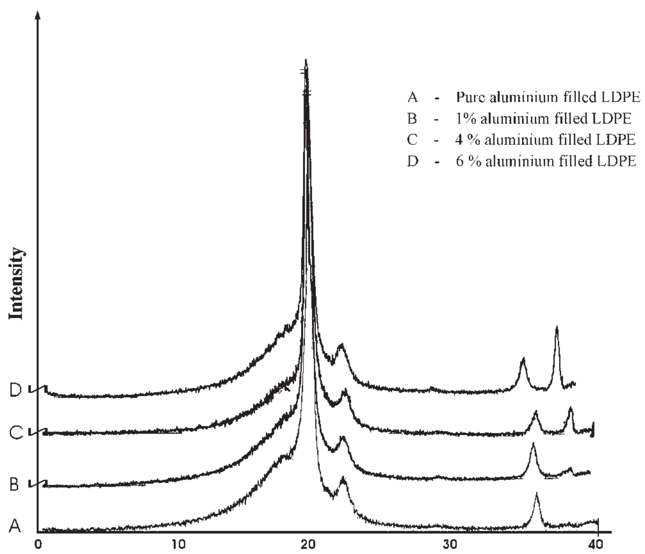

Figure 3 WAXD patterns of pure and Al-filled LDPE.

TABLE II
Crystallite Size for Different Peaks

Sample	Peaks observed approximately at				
	$2\theta = 19°$	$2\theta = 21°$	$2\theta = 23°$	$2\theta = 36°$	$2\theta = 38°$
Pure	20.14	80.82	54.17	167.76	–
1%	23.06	161.96	48.24	171.18	56.27
4%	117.48	44.95	203.34	278.82	168.78
6%	20.2	81.01	81.32	167.38	281.62

The graph (Fig. 2) is plotted between concentration of filler and density difference, which indicate that the density difference is maximum for 4% Al-filled LDPE and decreases for 6% Al-filled LDPE. The reason for this is given as that the number and size of voids for 4% Al-filled LDPE sample has increased. This is observed in micrographs of 4% Al-filled LDPE at both magnification.

WAXD patterns of pure and Al-filled LDPE

WAXD patterns for pure LDPE, 1% Al-filled LDPE, 4% Al-filled LDPE, and 6% Al-filled LDPE are shown in Figure 3.

In case of pure LDPE four peaks are observed at $2\theta = 19.01°$, $2\theta = 21.16°$, $2\theta = 23.45°$, and $2\theta = 36.05°$ in the range of $2\theta = 0–40°$. In case of 1% Al-filled LDPE, the peak at $2\theta = 21.16°$ (in case of pure LDPE sample) is found to have shifted to $2\theta = 21.34°$ and one more peak is observed in the nearby region at $2\theta = 21.51°$ and one additional peak appears at $2\theta = 38.47°$. The peak at $2\theta = 38.47°$ is found to be more intense for 4 and 6% Al-filled LDPE sample. In case of 4% Al-filled LDPE, three peaks are observed in nearby region at $2\theta = 21.34°$, at $2\theta = 21.46°$, and at $2\theta = 21.57°$. However in case of 6% Al-filled LDPE, single peak is observed in this region at $2\theta = 21.57°$. In case of all these filled samples, other peaks (observed for pure LDPE) are found to have shifted slightly.

A careful look at the values of 2θ indicates that near about all Al-filled LDPE composites show a slight shift in every peak. The reason for this is that the added Al powder enters into the crystalline region of LDPE samples, slightly modifying the crystal structure.

The additional peak at $2\theta = 38.47°$ is observed as Al filler is added into the sample and is found to be grown more prominently as concentration of filler

TABLE III
Values of Crystallinity and Filler Concentration

Concentration of Filler	Values of crystalline using Manjunath's formula
Pure	85.52
1% Al filled	87.58
4% Al filled	90.47
6% Al filled	87.12

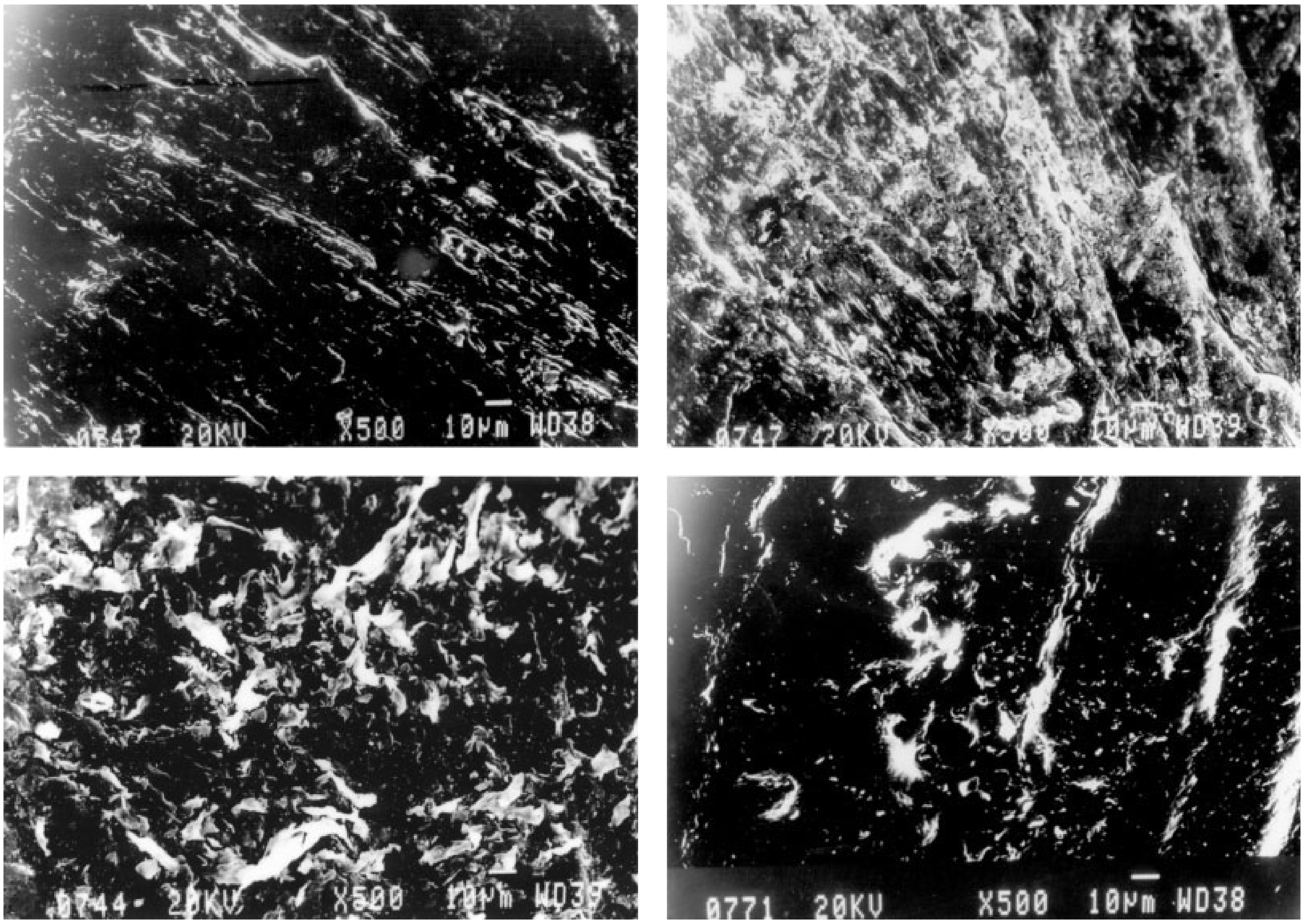

Figure 4 A: SEM of pure LDPE (at magnification ×500). B: SEM of 1% Al-filled LDPE (at magnification ×500). C: SEM of 4% Al-filled LDPE (at magnification ×500). D: SEM of 6% Al-filled LDPE (at magnification ×500).

increases. Hence this peak can be associated with the peak due to Al powder.

The values of crystallinity have been calculated and are tabulated (Table II). From the table it is evident that the values of crystallinity are nearly equal for 1% Al-filled LDPE and 6% Al-filled LDPE samples. A slight increase in crystallinity when compared with 1 and 6% Al-filled samples is observed for 4% Al-filled LDPE sample.

The values of crystallite size have been calculated and are tabulated (Table III). The crystallite size for 1% Al-filled LDPE is more than pure LDPE for all peaks. The crystallite size for 4% Al-filled LDPE sample is found to be maximum for three peaks. Thus, it is clear from the Table III that crystallite size has increased for all Al-filled LDPE composites. Crystallite size for peak $2\theta = 38^\circ$ (approximately) is found to have constantly increased as the concentration of added filler increases.

Structural morphologies of Al-filled LDPE

The micrographs of pure LDPE, 1% Al-filled LDPE, 4% Al-filled LDPE, and 6% Al-filled LDPE have been investigated using scanning electron micrograph and have been reported at two magnifications (×500 and ×2000) (Figs. 4 and 5).

In pure LDPE sample, the platelet-like structure, i.e. lamellar structure, has been observed with an average size of lamellae lying in between 8 (8×10^{-6} m) and 19 μm (19×10^{-6} m) at both magnifications. This observed structure and lamellar size closely agree with previously reported data.[12] Thus, different lamella are separated from each other by amorphous region and voids (present in very small number).

In 1% Al-filled LDPE, nearly about same structure is observed at lower magnification. The number of voids were found to have increased for this sample. For higher magnification, the structure is found to be slightly distorted. The average size of lamellae lie in between 4 (4×10^{-6} m) and 21 μm (21×10^{-6} m) at both magnifications.

In 4% Al-filled LDPE, the total structure is found to have disturbed. No platelet-like structure has been observed for both magnifications. But number and size of voids are found to have increased. This indicates that the additional Al powder has destroyed a well-organized crystalline pattern of

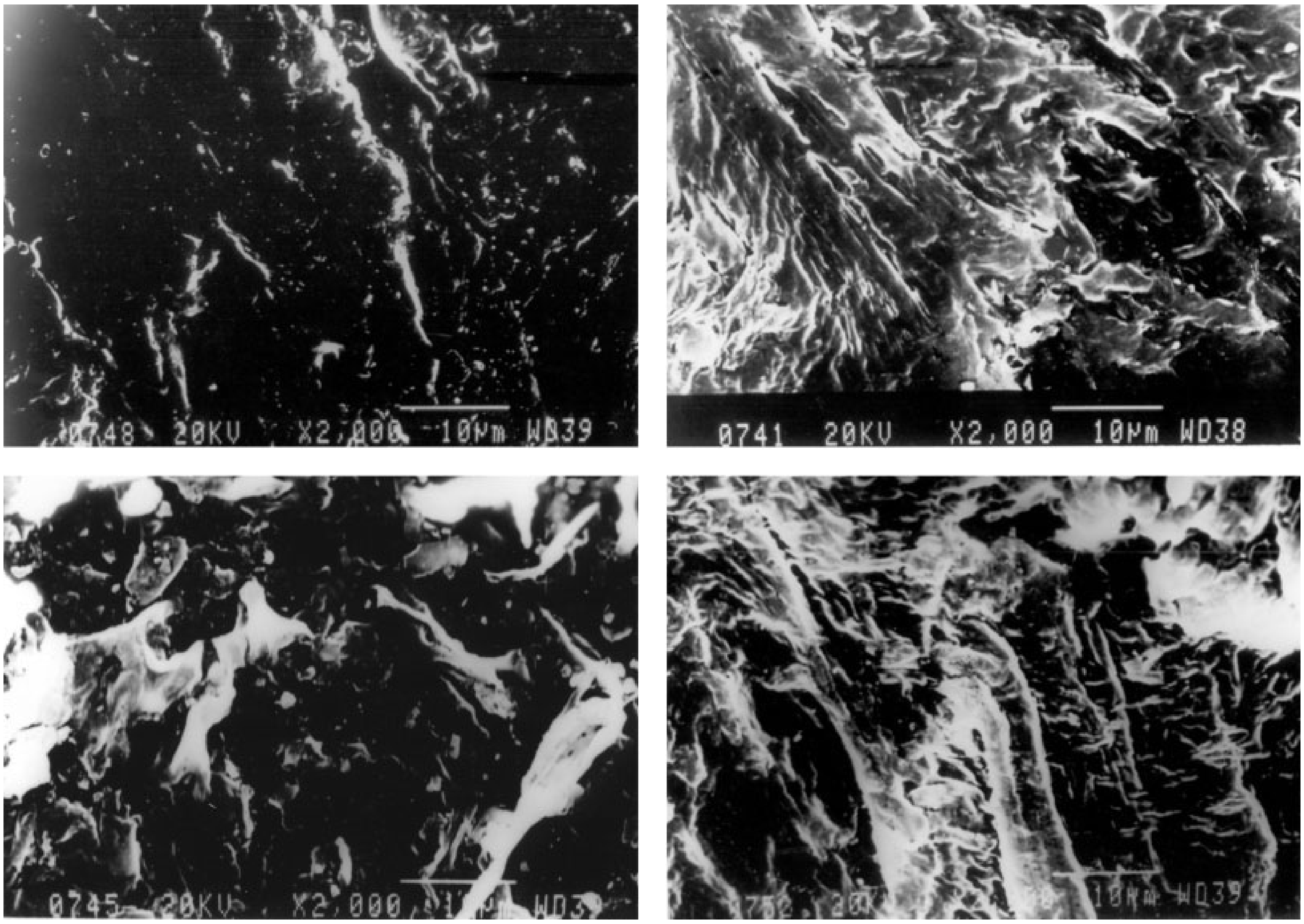

Figure 5 A: SEM of pure LDPE (at magnification ×2000). B: SEM of 1% Al-filled LDPE (at magnification ×2000). C: SEM of 4% Al-filled LDPE (at magnification ×2000). D: SEM of 6% Al-filled LDPE (at magnification ×2000).

LDPE (forming lamellae) and has a disturbed crystalline arrangement.

In 6% Al-filled LDPE sample, the morphological structure is just similar to that of pure LDPE for both magnifications with an average size of lamellae lying in between 5 (5×10^{-6} m) and 14 μm (14×10^{-6} m) for both magnifications. The crystallinity as well as crystallite size of pure and 6% Al-filled LDPE sample are also nearly same. This indicates that added 6% Al powder in LDPE sample occupies space in the voids formed during sample preparation.

Mechanical properties of Al-filled LDPE composites

Values of % strain at break, stress at break, load at break, and Young's modulus of pure LDPE and Al-filled LDPE samples have been tabulated (Table IV).

It is clear from the table that values of Young's modulus and load at break increase continuously from pure LDPE to 4% Al-filled LDPE sample but for 6% Al-filled sample the value of Y and value load at break approaches to that of pure LDPE. It is also clear from the table that the values of Y and load at break are maximum for 4% Al-filled LDPE.

The value of Y is found to have increased for 1% Al-filled LDPE. The reason for this increase in value of Y is associated with slight increase in crystallinity and crystallite size.

The values of Y and load at break are maximum for 4% Al-filled LDPE. The reason for this increase is resultant effect of increase in crystallinity and notable increase in values of crystallite size.

In case of 6% Al-filled LDPE, it is observed that the value of Y decreases when compared with that of 1 and 4% Al-filled LDPE samples. It should also

TABLE IV
Values of Strain at Breaks, Stress at Break, and Young's modulus (Y) of Pure and Aluminium-Filled Samples

Sample	% Strain at break	Stress at break	Young's modulus, Y (MPa)
Pure	34.95	2.81	94.49
1% Al	325.06	13.15	122.76
4% Al	251.51	14.41	159.20
6% Al	168.60	7.55	94.14

be noted that for 6% Al-filled LDPE sample the crystallinity as well as crystallite size are comparable with those in case of pure LDPE sample and are less as compared with 1% Al-filled LDPE and 4% Al-filled LDPE composites. From this observation it can be inferred that in case of 6% Al-filled LDPE composite the added Al powder gets collected in the voids, thus not affecting the crystallinity or the crystallite size. Thus Young's modulus and value of load at break have a value nearly equal to that of the pure LDPE sample. However, the values of stress at break as well as % strain at break have increased. This increase takes place in the same proportion and hence their ratio viz. Y remains unaffected in case of this sample.

CONCLUSION

Thus, it is clear from the results that by addition of small concentration of filler one can develop a material having good mechanical properties. This material can find applications in various areas. As LDPE is a commercially available low-cost material and added Al powder is having low concentration ($<10\%$), and thus the cost of the composite is automatically reduced.

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