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Morphological Study of PEG Added LDPE Porous Microparticles

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Absract

Porous Microparticles of Polyethylene Glycol (PEG) added Low Density Polyethylene (LDPE) were prepared by using a nanoprecipitation methods.PEG was used as an additive in LDPE in different weight keeping LDPE weight constant. The prepared powder samples were characterized by using Fourier transform infrared spectroscopy,X-ray diffraction, scanning electron microscopy.Fourier infrared transformation (FTIR) spectra confirmed the presence of PEG in LDPE and effect of PEG in LDPE was observed .The X- Ray Diffraction (XRD) pattern indicates the presence of PEG in LDPE matrix and absence of any extra peak in the pattern shows there is no new phase formation. The scanning electron microscopy images show that the concentration of Polyethylene Glycol decreased the agglomeration and increased the degree of sphericity of the polyethylene microparticles.

Keywords: LDPE/PEG microparticles, FT-IR, X-ray diffraction, SEM.

Introduction

Microparticles are defined as structures with dimensions less than 1000 µm and greater than 1 µm, which can also be obtained from biodegradable and non-biodegradable materials.A variety of materials can be used to prepare nanoparticles and microparticles by using different methods, e.g. nanoprecipitation, emulsion diffusion, double emulsion.[1]Polyethylene (PE) is a widely used plastic with tailorable properties based on molecular conformation with applications ranging from film packaging and electrical insulation to containers and piping. PE is characterized primarily based on density and the degree of molecule branching.In semi-crystalline materials, like polyethylene and polytetrafluoroethylene, the response of the material depends on molecular con-formation and volume fraction of crystallinity, in addition to temperature and strain rate. These materials can be thought of as molecular networks consisting of an amorphous phase containing entangled chains with the randomly oriented crystallite phase acting as physical cross-links.[2]

Nanoprecipitation, also known as antisolvent precipitation, desolvation, solvent displacement, and solvent shifting, was described by Fessi et.al.in 1989 and is a method for developing nanoparticles and microparticles[1] but the number of studies about nanoprecipitation of other polymers, including polyolefins, is limited. Because the method developed does not use additives such as surfactants, it affords particles without impurities that could induce adverse effects in organisms. Methods to control the size of\ particles produced by nanoprecipitation are needed.[3] Additionally, the method requires no or low surfactant concentration.[4]The main principle of nanoprecipitation technique is interfacial deposition of the polymer. Polymer interfacial deposition is formed after solvent addition, which is semipolar and miscible with water, displacement from lipophilic solution.[5]

Low Density Polyethylene is the most utilized petroleum-based synthetic polymer, due to its magnificent mechanical attributes, water holding capacity, lightness, cheapness and high energy effectiveness. LDPE owes its outstanding mechanical properties to its long and strong polymer chains or matrix.[6]Low density polyethylene (LDPE) is a tough and flexible polymer characterized by long branches that do not pack well into crystallites.[2] Low Density Polyethylene is among the most versatile polymers,but its uses are limited due to several drawbacks ,namely low strength, stiffness and poor heat resistance .To overcome these drawbacks and to prepare material with improved properties,fillers are incorporated into the matrix Fillers can affect the dimensional stability,crystallinity,mechanical and other properties of polymers.[7].

Here, we examined how varying the concentration of the polymer feedstock solution affects the diameter of LDPE microparticles prepared by nanoprecipitation methods

Materials and Methods.

Materials

Low density polyethylene (LDPE) is a soft, flexible, light weight plastic material was used as a matrix. Commercial grade LDPE with density 0.924gm/cm3, Xylene solvent of AR grade and PEG with average molecular weights 3500-4000 freezing point 56-60 °C and having PH in between 4.5 to 7.5[8].

Sample Preparation

Experimental Polyethylene microparticles were synthesized by nanoprecipitation method, 6.0 gm of LDPE polyethylene was dissolved in 40 ml of xylene using magnetic stirrer keeping temperature constant at 110 °C for two and half hour so as to obtain clear viscous solution. Then PEG was added to the solution of LDPE in different weight (1,3,5 and 7 gm). For maximum dispersion the solution was further stirred for two and half hour by keeping the temperature constant.The antisolvent for precipitation was 40 mL water placed in a beaker. The feedstock solution was injected into the antisolvent via a disposable syringe, with constant stirring 500 rpm. After drop by drop injection of the feedstock solution into the antisolvent. Fine microparticles were obtained and collected by filtration.

The morphology of the prepared particles was studied by using Fourier transform infrared spectroscopy (FT-IR),X-ray diffraction and scanning electron microscopy (SEM).

Results and Discussion

Fourier Transform Infrared Spectroscopy (FTIR):

FTIR is a spectroscopic method of analysis where IR rays are absorbed by bonds in a molecule. These IR ray’s energy can be related to the vibrational energy of different bonds found within different functional groups in a compound. LDPE containing different concentration of PEG (1, 3, 5 and 7 gm) is characterized by using FTIR spectroscopy

Figure 1: shows FTIR spectra of unadded LDPE and PEGadded LDPE

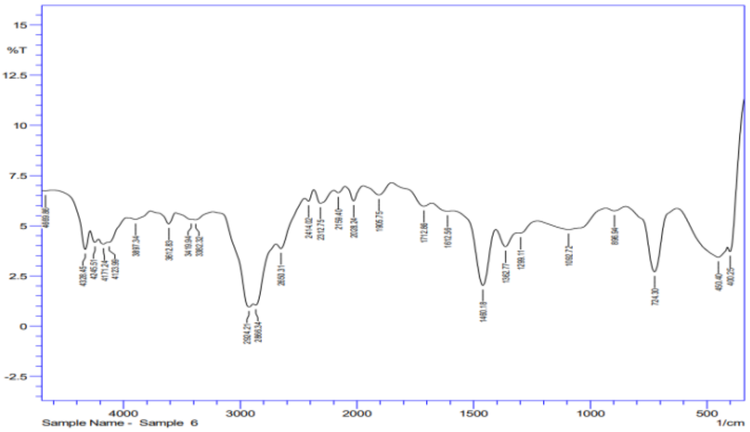
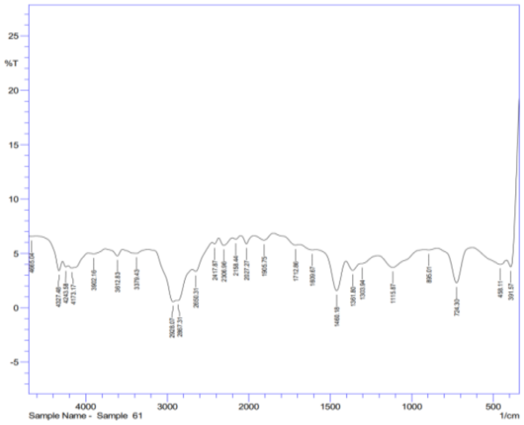


Fig.1(a) FTIR spectra of unadded LDPE



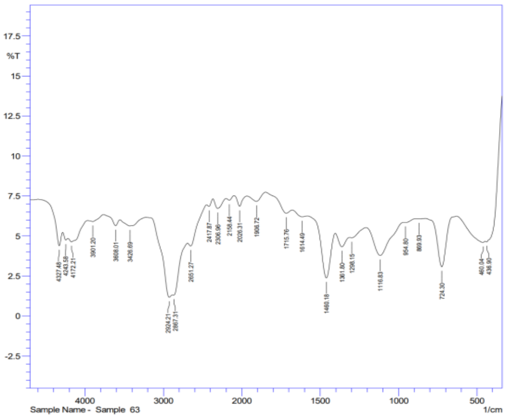


Fig.1(b) FTIR spectra of (PE-PEG/1)

Fig.1(c) FTIR spectra of (PE-PEG/3)

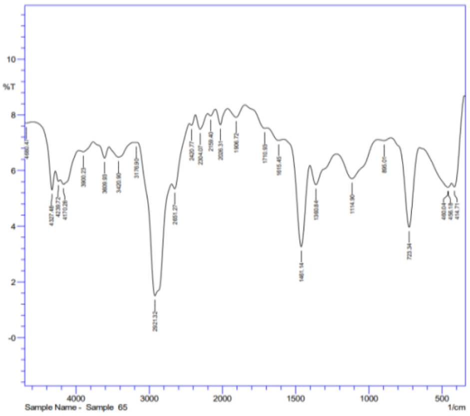


Fig.1(d) FTIR spectra of (PE-PEG/5)

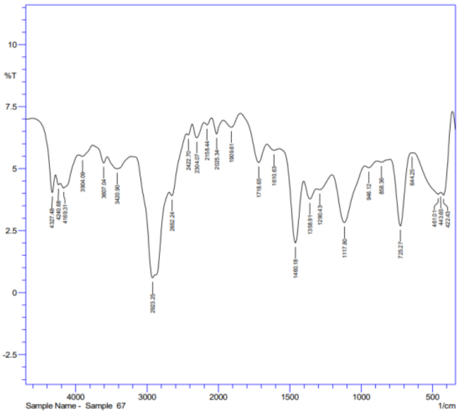


Fig.1(e) FTIR spectra of (PE-PEG/7)

Table 1:Analysis of FTIR spectra of unadded LDPE and PEG added LDPE samples

Sr.No.	Vibration	Frequency (cm^{-1})				
		PE	PE-PEG/1	PE-PEG/3	PE-PEG/5	PE-PEG /7
1	C-H Stretch of alkane	2924 & 2866	2928 & 2867	2924 & 2867	2921 & 2651	2923 & 2652
2	-CH_2- bend of alkane	1460	1460	1460	1461	1460
3	-CH_3 bend of xylene	1362	1361	1361	1360	1358
4	-C-O bond of PEG	1092	1115	1116	1114	1117
5	-OH bond of PEG	3612 to 3382	3612 to 3379	3608 to 3426	3609 to 3420	3607 to 3420
6	-C=C- bond of xylene	1612	1609	1614	1615	1610

From table 1 FTIR spectra of unadded LDPE show characteristics peaks at 2924.21 cm^{-1} and 2866.34 cm^{-1} due to asymmetrical and symmetrical CH stretching vibrations of LDPE respectively. The peak at 1460.18 cm^{-1} and 1362.77 cm^{-1} occured due to CH bending vibration and CH bending of CH3. The peak at 724.3 cm^{-1} due to C-H rocking (Asymmetric C-H bending). Peaks around in the spectra of 1115 cm^{-1} corresponds to the vibration of COC groups in PEG.Since PEG contains the functional group of the aliphatic ethers. The peak around 1610 cm^{-1} are due to alkene groups and represent unsaturated group from LDPE The peak around 1460 cm^{-1} are correspond to CH bending vibrations of methylene and methyl groups from LDPE and PEG.In LDPE spectrum a peak at 3420 cm^{-1} are corresponds to OH stretching vibrations of hydroxyl groups from PEG [7] The peak around 2924 cm^{-1} are correspond to CH stretching vibrations of methylene and methyl groups from LDPE and PEG .As PEG content increased, increase in the absorption peaks at 1115 cm^{-1}, corresponding to the stretching vibrations structure found in PEG.

The comparative study of FTIR spectra of unadded LDPE and PEG added LDPE microparticles was as follows, it is observed that there is slightly change in peak position for C-H stretch of alkane ,-CH2-bend of alkane.-CH3 bend of xylene,Peak position of -C-O bond of PEG was shifted to higher position It is observed that PEG added LDPE microparticles spectra contain one additional peak at 1115 cm^{-1} corresponding to PEG bond along with all the characteristic peaks of unadded LDPE spectra. There is also no significant shift in the characteristic transmittance peaks indicating that LDPE did not have strong interaction with PEG Since no noticeable change in peak positions except a slight variation in position of peaks which is due to some traces of additives i.e. polyethylene glycol. There is slightly change in peak position for-OH- bond of PEG and -C=C- bond of xylene.

Along with these peaks some other peaks are also observed in the spectra which correspond to -C=C- bond of xylene, -C-O bond of polyethylene glycol.

Wanchoo and Sharma [2003] proposes that the interactions that takes place between two or more chemical groups on different polymers theoretically should result in a shift of the peak positions of the groups present. Our results are in good agreement with this.The shift in peak position of the participating groups clearly be an indication that a sort of interaction exist between the matrix and the additives[9].

XRD Analysis of unadded LDPE and PEG added LDPE microparticle

X-RD study provides a wide range of information regarding crystallinity, phase change, crystal structure and its orientation of the materials including complex, polymer and salts.Figure 1(a) shows the XRD pattern for unadded LDPE microparticles.It shows dominant fairly sharp peak at 21.4° and a weak broad peak at 24.7° corresponds to (110) and (200) reflections from the orthorhombic polyethylene crystals arose from crystalline and amorphous regions in LDPE [7]

The sharp peak at nearly 2θ=21.33° was observed in unadded LDPE sample but the position of the same sharp peak in all PEG added LDPE sample was slightly shifted to their lower 2θ value.This is due to partial in corporation of PEG into LDPE microparticles.

Figure 2: shows XRD pattern of unadded LDPE and PEG added LDPE samples

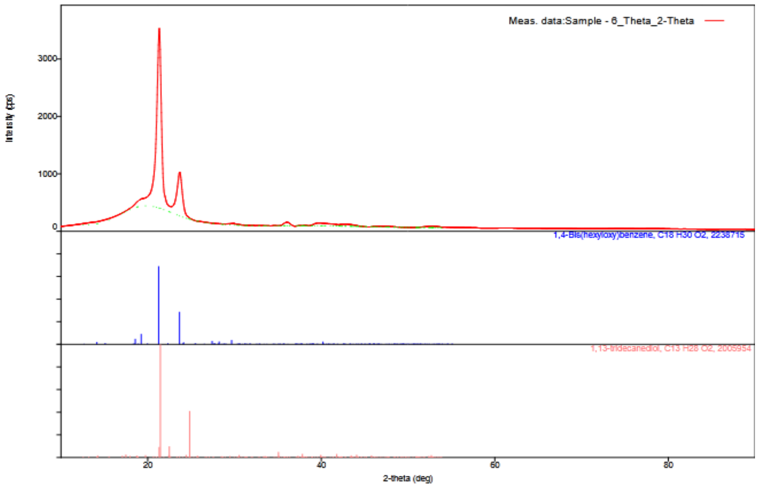


Fig.2(a) XRD pattern of unadded LDPE

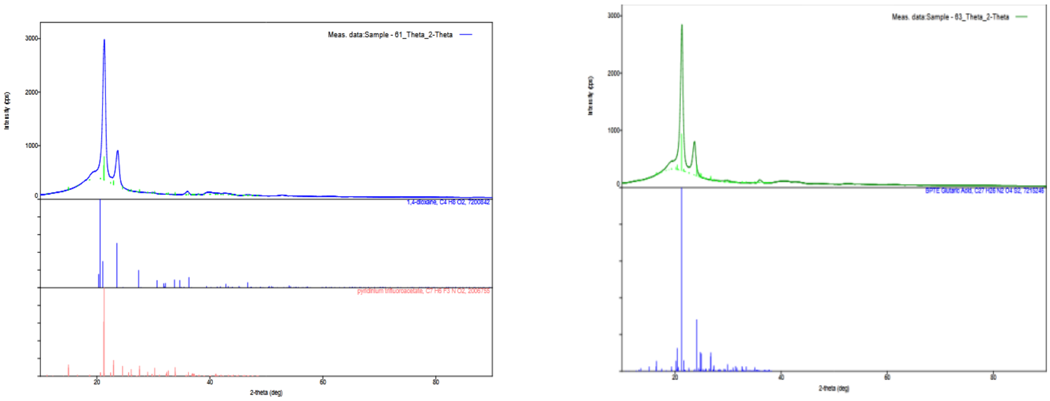


Fig.2(b) XRD pattern of (PE-PEG/1)

Fig.2(c) XRD pattern of (PE-PEG/3)

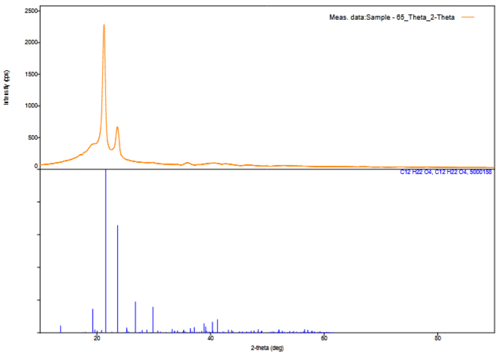


Fig.2(d) XRD pattern of (PE-PEG/5)

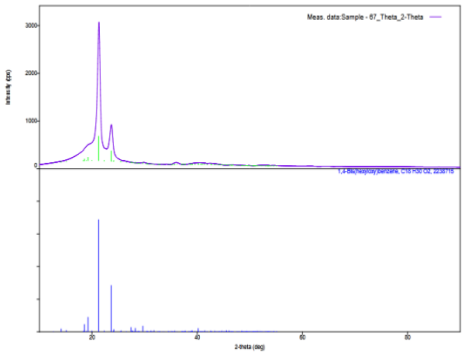


Fig.2(e) XRD pattern of (PE-PEG/ 7)

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The XRD pattern of LDPE shows crystalline phase along with amorphous phase but with the addition of PEG in LDPE changes crystallinity.The crystallinity was higher for unadded LDPE sample but with the composition of PEG in LDPE decreases the crystallinity.Debey Scherrer's formula was used to determine the particle size.calculated values for all samples are enclosed in table 2

$$D = \frac{0.9\lambda}{\beta cos\Theta}$$

Where, D = Crystal size
λ = Wavelength of X-ray
Θ = Bragg's angle in radian
β = Full width at half maximum

The crystal size of unadded LDPE 5gm and 7gm PEG added in 6gm LDPE was found to be 14.90 µm and 14.43 µm. Thus it is found that physically hinder crystal growth resulting in lower polymer crystallinity [8]

Table 2.XRD, 2θ and d-spacing values of unadded LDPE and PEG added LDPE

Sr. No.	**Sample code**	**Peak Position at 2θ**	**d-spacing**	**Crystal size(µm)**
1	PE	21.33°	4.1618	15.75
2	PE-PEG/1	21.30°	4.1674	14.74
3	PE-PEG/3	21.29°	4.1697	15.57
4	PE-PEG/5	21.24°	4.1789	14.90
5	PE-PEG/7	21.31°	4.1659	14.43

Scanning electron microscopy

The surface morphology of unadded LDPE and PEG added LDPE microparticles had been investigated using scanning electron microscopy (SEM) and are enclosed in figure 3.

Figure 3: shows the SEM images of unadded LDPEand PEG added LDPE

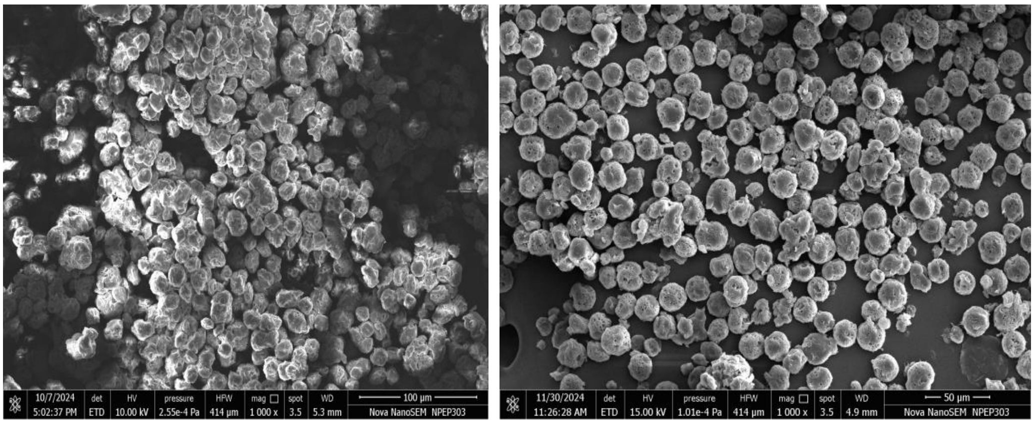

Fig.3(a) SEM images of unadded LDPE **Fig.3(b) SEM images of (PE-PEG/1)**

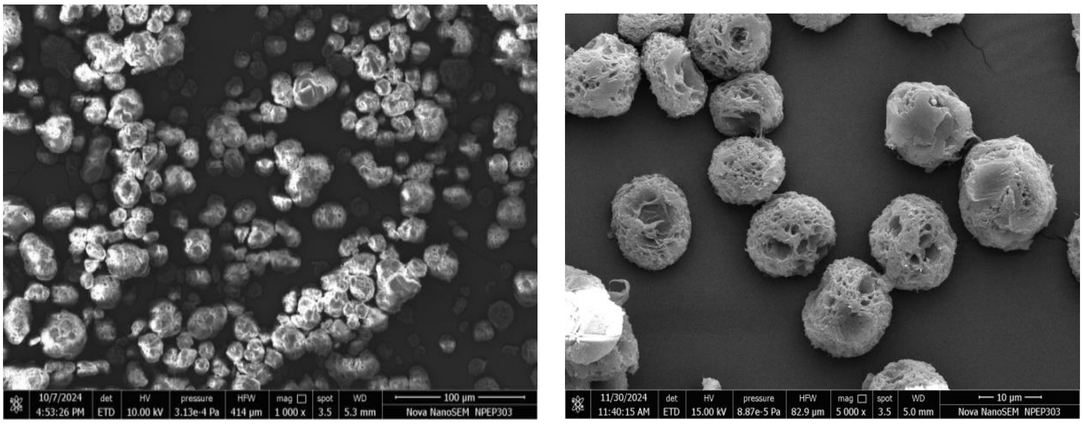

Fig.3(c) SEM images of (PE-PEG/3) **Fig.3(d) SEM images of (PE-PEG/5)**

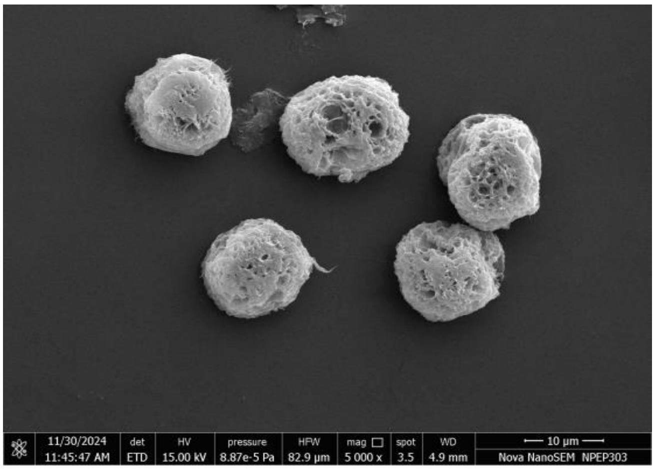

Fig.3(e) SEM images of (PE-PEG/7)

From figure3 it is observed that polyethylene microparticles are mostly spherical in shape with few irregularities, however in some samples agglomeration and non-porosity is observed. The factors affecting the porosity of microparticles are boiling point, solubility, surface area etc. of the porogen.Fig.3(a) shows the SEM image of PE.It is observed that, polyethylene microparticles having spherical shape with non-porous surface. The average particle size is ranging 10-50µm. slight agglomeration was observed for the polyethylene microparticles Fig. 3(b) shows the SEM image of 1gm

PEG added in 6gm LDPE shows that microparticles having spherical shape with few irregularities and rough surface. The average particle size is ranging between10-30µm .Fig.3(c) shows average particle size ranging from 11-25µm. the rate of agglomeration for the 3gm PEG added in 6gm LDPE microparticles was comparatively higher.Fig. 3(d) shows SEM image of 5gm PEG added in 6gm LDPE microparticles having spherical shapes with some irregularities and highly porous surface. The average particle size is ranging from 10-25 µm. slight agglomeration was observed in polyethylene microparticles. Fig. 3(e) shows the SEM image of 7gm PEG added in 6gm LDPE microparticles, it is observed that,microparticles have irregular shapes with few pores on the surface. The average particle size is ranging from 5-10 µm. slight agglomeration was observed in polyethylene microparticles.

Table 3:Analysis of SEM images of unadded LDPE and PEG added LDPE

Sample	Particle size (µm)	Porous / Non-Porous
PE	10-50	Non-porous
PE-PEG/1	10-30	Non-porous
PE-PEG/3	11-25	Non-porous
PE-PEG/5	10-25	Porous
PE-PEG/7	5-10	Porous

The variation of particle size depends on percentage of additive.Table 3 enclosed the values of average particle size of unadded LDPE and PEG added LDPE microparticles..

Conclusion

Polyethylene microparticles containing different amount of Poythylene glycol were prepared by nanoprecipitation method.

Results of the particle size calculated by using Debey Scherrer's methods and SEM are found to be nearly same.They are found to be in the range.Slight porosity was observed in sample containing 5 g and 7gm polyethylene glycol. It might be due to hydrogen bonding between PEG or might be due to other chemical interaction (such as esterification), which led to decrease in surface area and showed porosity.The average particle size ranges between 2-20µm. All the particles have nearly the same size for PE-PEG/1 and PE-PEG/3 samples.Thus particle size of LDPE can be controlled by addition of specific amount of PEG. Percentage of PEG in LDPE affects the particle size of PE.Remarkable effects is observed for 7gm PEG added LDPE sample.it lowers the size of PE microparticles.

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