Structural and Thermal Studies of PGA/LDPE Microsphere

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Abstract: Low density polyethylene (LDPE) microsphere doped with different amount of polyglycolic acid (PGA) is synthesized by chemical decomposition method. A synthesized microsphere is structurally characterized by X-ray diffraction, FT-IR and scanning electron microscopy. From the data it is observed that, PGA/LDPE microparticles are amorphous having spherical surface with few irregularities. Formation of PGA/LDPE is confirmed by FT-IR. Thermal decomposition of PGA/LDPE microspheres is studied with the help of TGA and DSC and its density was determined by powder bulk method. Antimicrobial activity is also tested for PGA added LDPE microparticals against E.coli and P.acne to check their bioactivity. The rate of drug release by microparticles (PGA/LDPE) was tested for amoxicillin trihydrate.

Keywords: PGA/LDPE microsphere, X-ray diffraction, FT-IR, TGA and bioactivity.

Introduction

Low density polyethylene (LDPE) microspheres are commonly used as permanent or temporary filler. Lower melting temperature enables polyethylene microspheres to create porous structures in ceramics and other materials. High sphericity of polyethylene microspheres, as well as availability of colored and fluorescent microspheres, makes them highly desirable for flow visualization and fluid flow analysis, microscopy techniques, health sciences, process troubleshooting and numerous research applications. Charged polyethylene microspheres are also used in electronic paper digital displays. [1-2]

Experimental

Polyethylene macroparticles are synthesized by chemical decomposition method, 6.0404 gm of polyethylene bag pieces and polyglycolic acid (0.3, 3, 5 and 7 gm)was taken in 40 ml xylene. The mixture was stirred for 20-30 min at 100^{O} C on magnetic stirrer to obtain a homogeneous gel. Then gel was pour on plane substrate to form a thick film. It was cooled at room temperature for 24 hrs. Then dried gel was collected and ground to form a fine powder.

Result and discussion

Structural characterization

X-ray diffraction

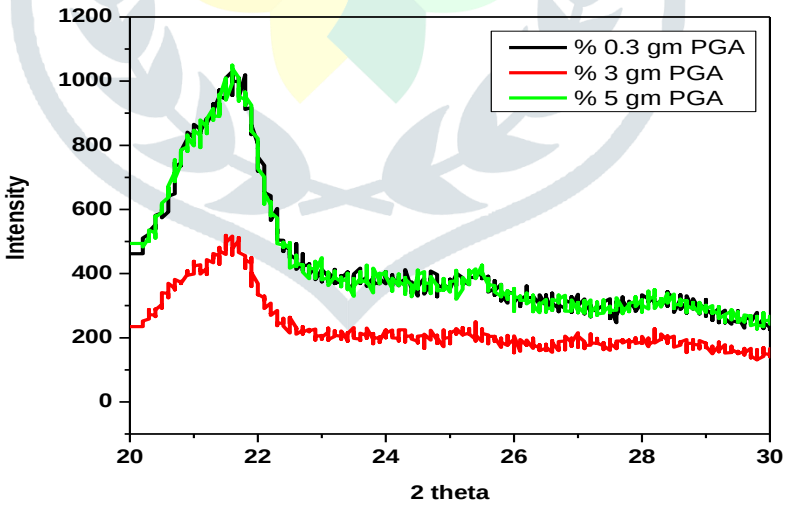
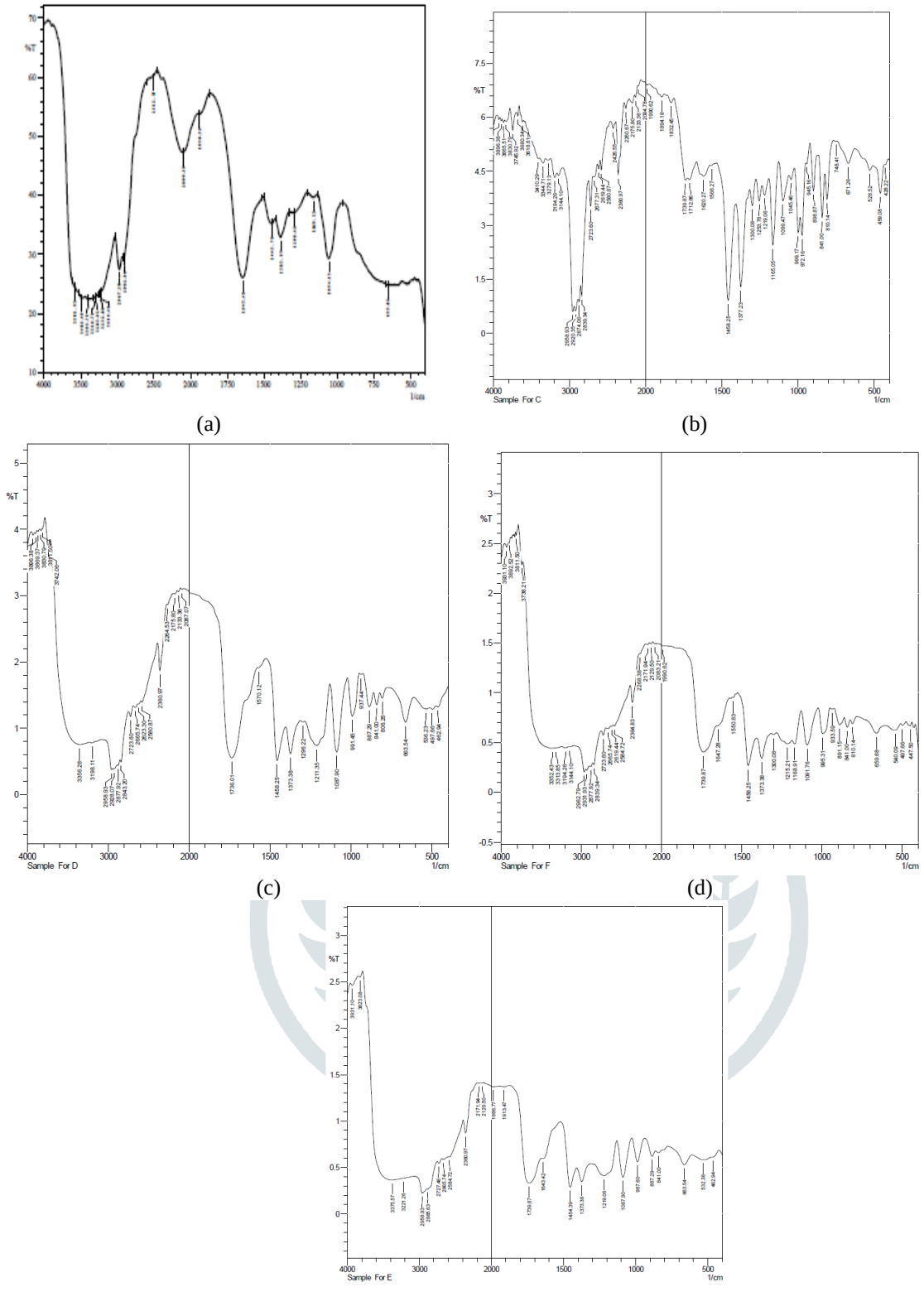


Figure 1: XRD of a] PE-PGA/0.03, b] PE-PGA/3 and c] PE-PGA/5

Figure 1 Shows XRD pattern for the a) PE-PGA/0.3, b) PE-PGA/3 and c) PE-PGA /5. It shows amorphous nature of LDPE/PGA microparticles. A broad peak correspond to $2\theta = 21.58^{o}$, 21.0^{o} and20.83^{o} for PE-PGA/0.3, PE-PGA/3 and PE-PGA /5 respectively. The broad peak appearing reveals that polyethylene microparticles were amorphous in nature [3-4]. It is observed that, as the concentration of PGA increases angles shifted towards lower value i.e. Blue Shift. This may be due to change in composition of microparticles.

Fourier Transform Infrared Spectroscopy (FTIR):



(a) (b) (c) (d) (e)

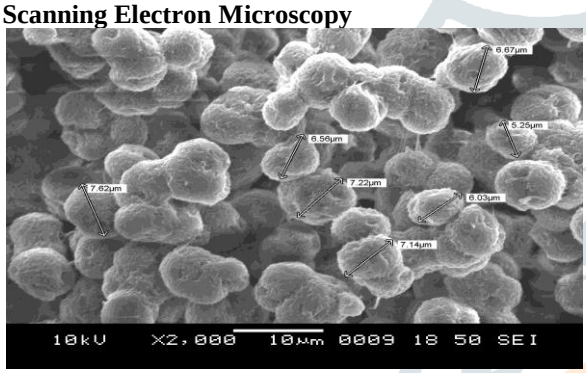
Fig 2: FT-IR spectra for the a)PE-PGA/0.1, b) PE-PGA/0.3, c) PE-PGA/3, d) PE-PGA/5, e) PE-PGA/7

From the FT-IR spectra (figure 2) for the PGA/LDPE microparticles, all the samples show the two characteristic peaks in the range of 2877-2967 cm^{-1} which corresponds to C-H bend of alkane. And another characteristic peak near 1445-1458 which corresponds to $–CH_2-$ bend in alkane. These peaks confirm the formation of polyethylene microparticles. Table 1 shows the comparative study of frequency co-relation for PGA/LDPE microparticles containing different amount of PGA (0.1, 0.3, 3, 5, and 7 gm). It was clear that their no remarkable change in peak position and intensity of bonds except a slight variation in position of peaks is due to some traces of additives i.e. PGA. Our results are in good agreement with the reported research [5-9]. Along with these peaks some other peaks are also observed in the spectra which corresponds to –C=C- bond of xylene, -C=O bond of PGA.

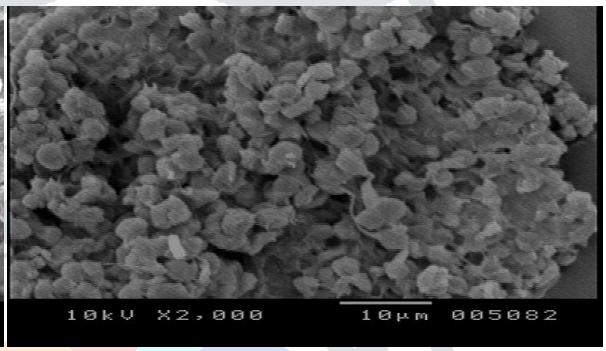
S.No.	Vibration	Frequency (cm^{-1})				
		PE-PGA/0.3	PE-PGA/3	PE-PGA/7	PE-PGA/5	PE-PGA/0.1
1	C-H Stretch of alkane	2958 & 2920	2958 & 2928	2885 & 2958	2877 & 2962	2902 & 2967
2	$-CH_2-$ bend of alkane	1458	1458	1454	1458	1445
3	$-CH_3$ bend of xylene	1377	1373	1373	1373	1383 cm^{-1}
4	-C-O bond of PGA	1165	1087	1087	1091	1160
5	-OH bond of PGA	3144 to 3194	3198 to 3356	3221 to 3375	3221 to 3375	3216 to 3581
6	-C=C- bond of xylene	1620	1570	1643	1647	1643
7	-C=O bond of PGA	1739	1736	1739	1739	-

Table 1: frequency correlation table for PE microparticles

Scanning Electron Microscopy



(a)



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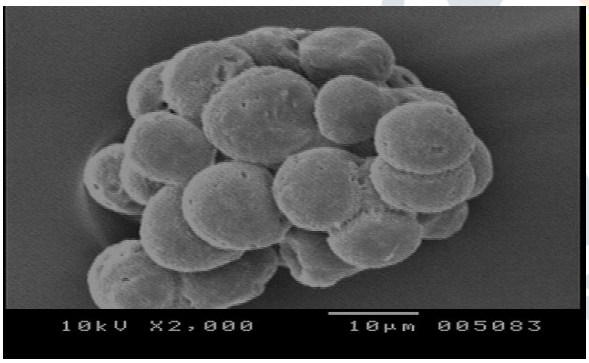

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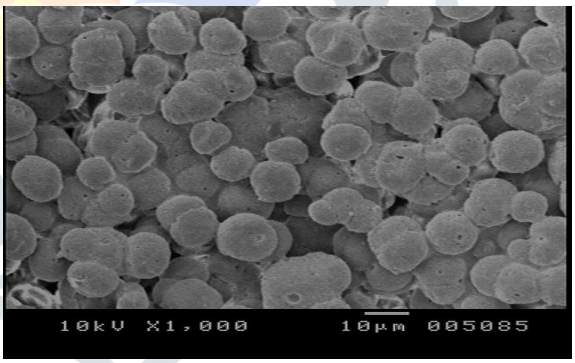

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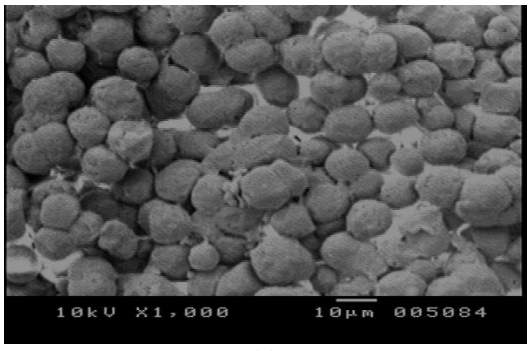


(e)

Figure 3: SEM images of (a) PE-PGA/0.1, (b) PE-PGA/0.3, (c) PE-PGA/3, (d) PE-PGA/5 and (e) PE-PGA/7

Figure 3 shows the SEM pictures of PGA-LDPE microparticles using different concentration of polyglycolic acid (0.1, 0.3, 3, 5 and 7 gm) as additive. From SEM pictures of PE-PGA/0.1, PE-PGA/0.3, PE-PGA/3, PE-PGA/5 and PE-PGA/7 microparticles, 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.

The particle size PE-PGA varies with the addition of PGA in PE. The particle size is minimum i.e. in the range 2-6 µm for PE-PGA/0.3 sample. The variation in size of the particle is maximum for PE-PGA/5 (8-22 µm) and PE-PGA/7 (6-15 µm). The variation in size of microparticle is minimum (or nearly uniformed sized microparticle) for PE-PGA/0.3 and PE-PGA/3 samples.

Thermal Characterization

Differential Scanning Colorimetry (DSC)

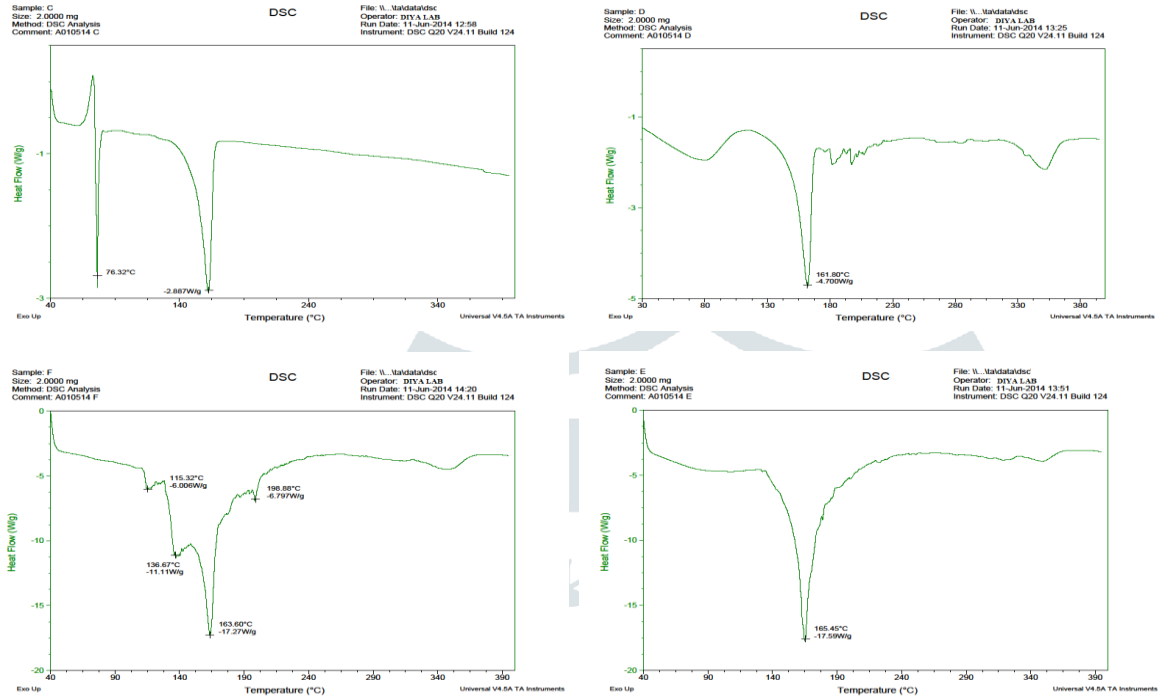


Figure 4: DSC curve for (a) PE-PGA/0.3 (b) PE-PGA/3 (c)PE-PGA/5 (d)PE-PGA/7

Figure 4 Show the DSC curves of PGA/LDPE microparticles having different concentration of polyglycolic acid 0.3, 3, 5 and 7 gm respectively as an additive.

Sharp endothermic peak of PE-PGA/0.3, PE-PGA/3, PE-PGA/5 and PE-PGA/7 shows the formation of liquid crystals. Graph for sample PE-PGA/5shows number of peaks indicating the melting of sample with decomposition. Graph of sample PE-PGA/3 shows one small concave peak at 350^0C shows eutectic impurity.

From the table 2 and figure 4d, it is determined that in PE-PGA/7 sample amount of PGA (7 gm) is maximum and therefore it shows higher negative value of heat flow -17.59w/g at temperature 165.45^0C.

Sample PE-PGA/0.3 contain less amount of PGA (0.3gm) than PE-PGA/3, PE-PGA/5and PE-PGA/7, thus in figure 4a, it is observed that the endothermic peak for sample PE-PGA/0.3 obtained at minimum temperature 76.32^0C with heat flow -2.887w/g.

In figure 4a and 4b of sample PE-PGA/0.3 and PE-PGA/3 shows peak near about at same temperature 161.74^0C and at 161.80^0C respectively, but values of heat flow are different, for PE-PGA/0.3 is -2.887w/g and for PE-PGA/3, -4.700w/g this is because of the presence of 3gm of PGA in PE-PGA/3.Curves in these graphs also determine heat of fusion and melting points. With the help of above data we are able to analyze molecular interaction.

From the above data it clearly shows that, the addition of different amount of PGA samples show different values of heat flow and temperature. The above information is very useful for knowing thermal properties like melting point, heat of fusion and molecular interaction.

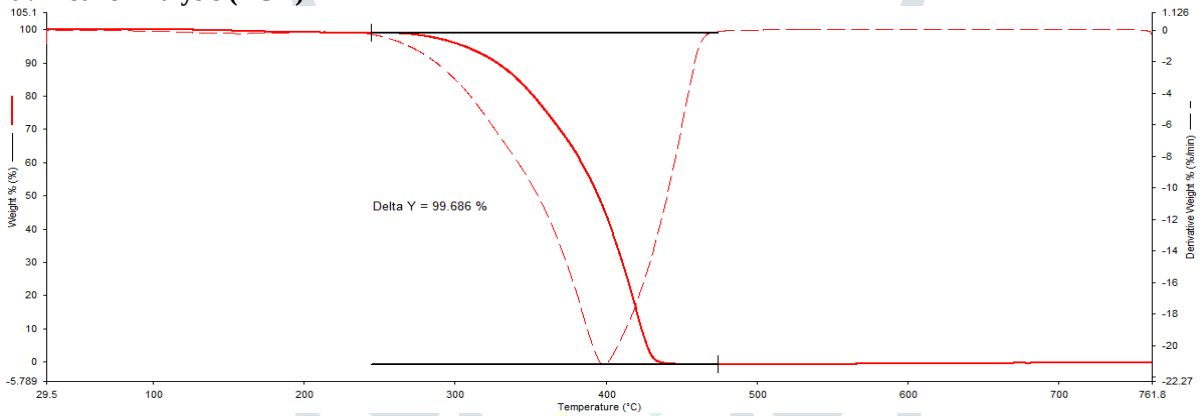
Table 2: Heat flow and transition temperature.

Sr. No.	Sample	Heat flow	Temperature	T_g (°C)
1	**PE-PGA/0.3**	-2.887w/g	76.32^{0}C	70
2	**PE-PGA/3**	-4.700w/g	161.80^{0}C	92.5
3	**PE-PGA/5**	-6.006w/g -11.11w/g -17.27w/g -6.797w/g	115.32^{0}C 136.67^{0}C 163.60^{0}C 198.88^{0}C	127
4	**PE-PGA/7**	-17.59w/g	165.45^{0}C	115

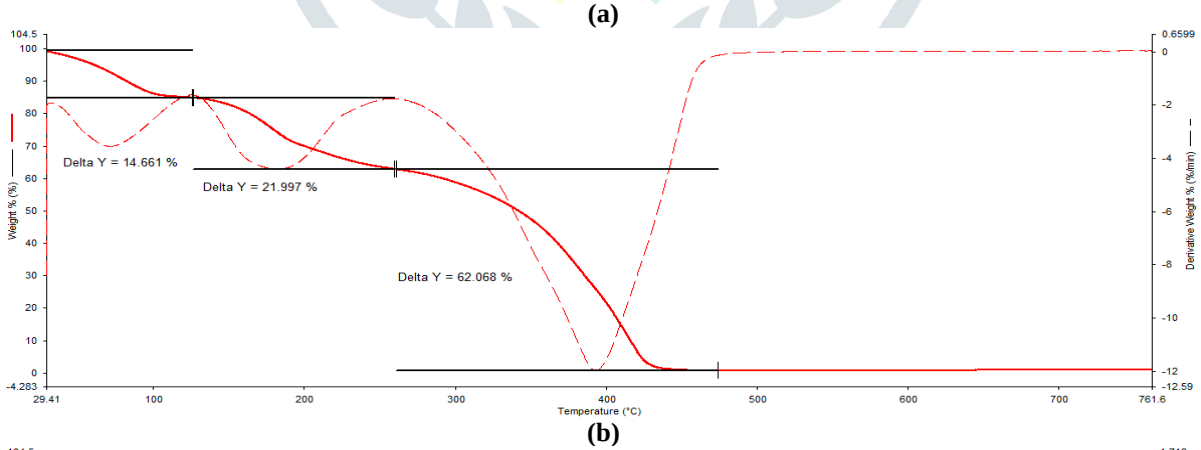
Data of DSC for PE-PGA/0.3, PE-PGA/3, PE-PGA/5 and PE-PGA/7, has summarized in table 6.5. Which shows the heat flow and decomposition temperature and glass transition temperature for PE-PGA/0.3, PE-PGA/3, PE-PGA/5 and PE-PGA/7 [10].From the data, it is observed the transition temperature increases with increasing amount of PGA upto 5 gm, on further addition of PGA glass transition temperature shifted to lower temperature.

In table 2, heat flow in all the samples show –ve value. In an endothermic process such as most phase transitions, heat is absorbed and therefore heat flow to the sample is higher than that to the reference hence $\Delta\frac{dH}{dt}$ is positive. Other endothermic process includes helix, dehydration, reduction reaction and some decomposition reactions. In exothermic process, crystallization, some cross linking process, oxidation reaction and some decomposition reaction the opposite is true and $\Delta\frac{dH}{dt}$ is negative.

Thermogravimetric Analysis (TGA)



(a)



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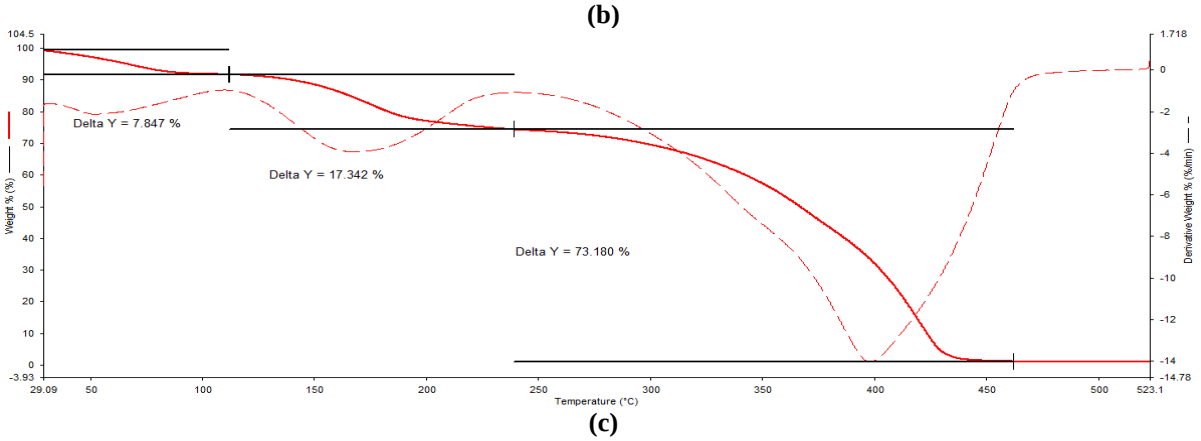

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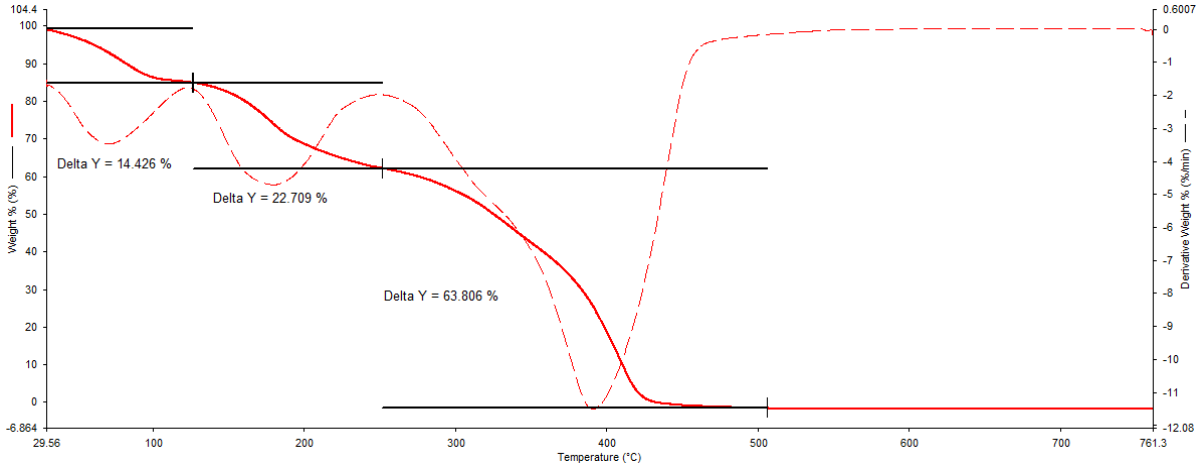

(d)

Figure 5: TGA curve for (a) PE-PGA/0.3 (b) PE-PGA/3 (c) PE-PGA/5 (d) PE-PGA/7

Table 3: Weight loss of PE-PGA microparticles.

Sample	On set temp.(T_1)	Peak temp.(T_2)	Weight loss (%)	Residual at peak temp.
PE-PGA/0.3	250 °C	480 °C	99.686	0.314 °C
PE-PGA/3	a) 80 °C b) 123°C c) 253°C	120°C 250°C 460°C	7.847 17.342 73.180	1.631°C
PE-PGA/5	a) 83°C b) 130°C c) 274°C	130°C 270°C 480°C	14.661 21.997 62.066	1.336°C
PE-PGA/7	a) 86°C b) 143°C c) 282°C	140°C 280°C 493°C	14.426 22.709 63.860	-0.941°C

From the thermograms it is observed that thermal curve is displayed from left to right. The descending TGA thermal curve indicates a weight loss occurred. These are caused by chemical reaction like decomposition, loss of water of crystallization and combustion. And also due to physical transitions vaporization, evaporation, sublimation, desorption and drying.

PE-PGA/0.3 sample shows degradation at temperature 240^0C, PE-PGA/3 shows degradation at temperature 110^0C and 240^0C similarly PE-PGA/5 shows degradation at temperature 110^0C and 250^0C and sample PE-PGA/7 degraded between temperature 90^0C and 160^0C. From this data it is cleared that sample PE-PGA/7 starts degradation at minimum temperature this might be due to highest amount of PGA (7gm) in polyethylene. Samples PE-PGA/3, PE-PGA/5 and PE-PGA/7 show multistep decomposition whereas sample PE-PGA/0.3 shows thermal decomposition with the formation of gaseous reaction product.

From the above discussion it is concluded that addition of PGA in polyethylene, the degradation or decomposition pattern changes and the thermal stability decreases, our results are in good agreement with [10].

Conclusion

Polyethylene microparticles containing different amount of polyglycolic acid has prepared in xylene by chemical decomposition method. As synthesized PE-PGA microparticles are structurally characterized by X-ray diffraction. All the samples show a broad peak nearly at 2θ=21°and confirms amorphous nature of microparticles. Slight variation in peak position is observed, due to different concentration of polyglycolic acid. Formation of PE-PGA microparticles were confirmed by FT-IR spectroscopy.

Surface morphology of polyethylene microparticles was estimated by SEM. It shows irregular shape with non-porous surface for all samples, slight porosity is observed in sample containing 5 g polyglycolic acid. The particle size ranges between 2-22 µm. All the particles have nearly the same size for PE-PGA/0.3 and PE-PGA/3 samples.

PE-PGA microparticles were thermally characterized by differential scanning colorimetry and thermogravimetry. For all samples of PE-PGA/0.1, PE-PGA/0.3, PE-PGA/3, PE-PGA/5 and PE-PGA/7show endothermic peaking DSC when decomposition occurs. Heat flow increases with increase in the concentration of polyglycolic acid. PE-PGA/5 shows more endothermic peaks with more heat flow at higher temperature.

The descending TGA thermal curve indicates a weight loss occurred. Sample PE-PGA/3, PE-PGA/5and PE-PGA/7 show multistep decomposition whereas sample PE-PGA/0.3 show thermal decomposition with the formation of gaseous reaction product. From TGA It is observed that, with increase in concentration of PGA degradation temperature decreases but sample PE-PGA/5show highest degradation temperature, but it is lower than polyethylene microparticles.

References

1. Hausberger AG, DeLuca PP.;"*Characterization of biodegradable poly (D,L-lactideco-glycolide) polymers and microspheres*" **J Pharm Biomed Anal.; 13; pp747- 760; 1995**.
2. Kostanski JW, DeLuca PP. "*A novel in vitro release technique for peptidecontaining biodegradable microspheres*". **AAPS PharmSciTech. 2000;1: Available from: http://www.pharmscitech.com**
3. ErsenGöktürk, HüseyinErdal; "*Biomedical applications of polyglycolic acid (PGA)*"; **SakaryaÜniversitesi Fen BilimleriEnstitüsüDergisi; 21(6);pp1237-1244; 2007**.
4. N. Sanjeeva Murthy, "*Recent Developments In Polymer Characterization Using X-Ray Diffraction*";**The Rigaku Journal;21(1); pp 15–24; 2004**.

5. W. L. Oliani, D. M. Fermino, Luiz Gustavo Hiroki Komatsu, AdemarBenevoloLugao, Vijaya Kumar Rangari, NiltonLincopan and DuclercFernandes Parra ; "*Preparation and Characterization of Polyethylene Nanocomposites with Clay and Silver Nanoparticles*";**The Minerals, Metals & Materials Series; Springer; pp-701-718; 2017.**
6. J. V Gulmine, P. R Janissek, H. M Heise, L Akcelrud; "*Polyethylene characterization by FTIR*"; **Polymer Testing; 21(5); pp 557-563; 2002**.
7. S. Krlmm, C. Y. Liang, G. B. B. M. Sutherland and Harrison M. Randall; "*Infrared Spectra Of High Polymers. Ii. Polyethylene*";**The Journal Of Chemical Physics; 25(3); Pp 549-562; 1956.**
8. JULIE CHARLES And G.R. RAMKUMAAR; "*Qualitative Analysis Of High Density Polyethylene Using FTIR Spectroscopy*"; **Asian Journal Of Chemistry; 21(6); pp 4477-4484; 2009.**
9. Ronald P. D'amelia, Samantha Gentile, William F. Nirode, Ling Huang, "*Quantitative Analysis Of Copolymers And Blends Of Polyvinyl Acetate (Pvac) Using Fourier Transform Infrared Spectroscopy (Ftir) And Elemental Analysis (Ea)*";**World Journal Of Chemical Education; 4(2); pp 25-31; 2016**.
10. L. contat-Rodrigo, A. Ribes-Greus, C.T. Imrie; "*Thermal Analysis of high density polyethylene and low density polyethylene with enhanced biodegradability*"; **Journal of applied polymer science; 86(3); 2002**.