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Effect of Different Sterilization Methods on Biodegradation of Biomedical Polypropylene

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Abstract

The aim of the present work is to study the effect of different sterilization methods on the biodegradation of biomedical polypropylene (PP) under the same biotic conditions. Three different sterilization techniques; γ-irradiation, steam sterilization and UV-irradiation were used to compare the effect of different sterilization methods on the biodegradability of PP. Neat and sterilized samples were incubated in compost and fungal culture environments. The changes in functional groups, mechanical properties, surface morphology and intrinsic viscosity in polymer were characterized by FT-IR spectroscopy, Instron, SEM and viscometric measurements, respectively. It was observed that the biodegradation of γ-sterilized samples in composting and microbial culture environments was higher than UV-irradiated samples, while UV-irradiated more than steam-sterilized and neat samples. The results showed that the radio and photo-oxidative pretreatment directly enhanced the biodegradability of PP as the increase in fungal growth rate and weight loss during composting was found. The biodegradation rate of PP at the same biotic conditions mainly depends on the rate of degradation that initially occurred during sterilization. Overall, this study demonstrated that the biodegradation of sterilized PP in biotic conditions significantly depends on the nature of sterilization method.

Keywords: Biomedical polypropylene; Biodegradation; Sterilization methods; Composting; Fungal culture

Introduction

The unique properties of polyolefins such as durability, transparency, mechanical properties, low cost, resistance to weathering and photo-degradation as well as biological attack and hydrophobicity, have contributed to their skyrocketing utility in different applications. In practice, any change of the polymer properties relative to the initial desirable properties is called "degradation". In this sense, degradation is a generic term for any number of reactions that are possible in a polymer. The degradation of polymers involves several physical and/or chemical processes accompanied by structural changes which lead to significant deterioration of the quality of the polymeric materials (i.e., worsening of its mechanical) and finally to the loosening of its functionality. In a finished product, such change is undesirable. However, degradation can be useful for recycling/reusing the polymer waste to prevent or reduce environmental pollution. A number of factors are responsible for the deterioration of the polymer properties, such as oxidative and thermal degradation, photo irradiation, high-energy irradiation, biological, chemical and climate factors, etc.; all these factors limit their service life. The initiating or degrading agent defines the type of degradation, hence the degradation of polymer mainly classified as bio-, thermo-, photo-, and radio-oxidative/degradation. The degradation process of the polymer has specific mechanism and depends on the type of degrading agent and the nature of macromolecular chain and structure.

Polypropylene (PP) is widely used in the manufacturing of medical disposables (such as syringes, catheters, vials, blood transfusion bags, and dialyzers for blood purification etc.) and increasingly applied in the pharmaceutical and food packaging, where the material is mostly sterilized. Sterilization defined as many processes which results in total destruction of all forms of microbial organism. There are many different sterilization techniques (chemical, heat and radiation sterilization processes) depending on the purpose of the sterilization and the material that will be sterilized. Sterilization processes should be capable of sterilizing biomedical polymers without adversely affecting their quality or properties. There is no single sterilization method can sterilize all polymers without some damage or degradation because every method has some advantages and disadvantages. The choice of the sterilization method alters depending on polymeric materials for giving less harm. The use of either chemical sterilization (mostly ethylene oxide), or heat sterilization (steam or dry heating) or radiation sterilization (β/electrons or gamma radiation), polymer materials undergo a series of oxidative reactions that lead to chemical, physical and mechanical degradation. The degradation of sterilized medical plastics continues for a long time during their shelf life and service, this process called post-degradation or post-sterilization. Some authors [1-3] have previously studied the effect of steam sterilization on PP. It was reported that steam sterilized PP at 121°C undergo changes in the crystalline structure mostly post-crystallization and physical aging effects [1], while no significant effect on the molecular structure was observed at this temperature [2,3]. Currently most of medical plastics sterilized by γ-radiation, which is used when materials are sensitive to the high temperature of autoclaving. The most commonly validated dose used to sterilize medical devices is 2.5 Mrad [4]. This process is replacing the hazardous and environmentally destructive use of ethylene oxide, which is vented into atmosphere. However, sterilization of medical plastics using γ-radiation is also known to result in physical changes including embrittlement, discoloration, and decreases in molecular weight [5-8]. The modern alternative sterilization processes such electron irradiation and UV-irradiation can form radicals in the

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polymer, resulting similar degradation effects as the γ-radiation process [1]. UV-irradiation successfully applied for sterilizing packaging materials especially after the development of more powerful sources of UV radiation [9]. The microbicidal effects of UV-irradiation lies in the range of 200–315 nm, with an optimal effect being between 250 and 280 nm. UV light at a wavelength of 253.7 nm is an effective germicide against yeast, moulds, bacteria, viruses and algae [10]. The lethal irradiation dose defined as the product of irradiation intensity and time and expressed in terms of milli Watts second per square centimeter (mW s cm^{-2}). A typical UV radiation intensity is between 0.5 and 1.5 W cm^{-2} at a distance of 10 cm. Recently, it was found that sterilization using hydrogen peroxide followed by UV irradiation is effective and accepted method for industrial application [10].

Since sterilization methods mostly cause degradation/post-degradation, such disadvantage could become an advantage from the environmental point of view. Consequently, the pretreatment of sterilization to accelerate the biodegradation of disposables medical plastics has become an interested topic [11,12]. Some plastic wastes can be recycled to produce other products while the medical plastic wastes cannot be recycled due to their pathological and infection considerations. Thus, medical plastic wastes are mostly incinerated. Incineration of plastics, which needs higher energy, input and emits toxic gases into the atmosphere. It requires more land-space and finding of acceptable sites for land-filling near urban areas is becoming difficult and involves health risks due to infectious wastes and need of proper biomedical waste management [13]. However, from an economic and health aspect plastics, which disappear in soil, would be an environmentally acceptable method [14]. Biodegradation can be an alternative to overcome the problem of plastic waste disposal. Biodegradation is caused mainly by enzymes which produced by microorganisms such as bacteria, fungi and algae. Biodegradation of plastics depends on different factors such as the compost (constitution, temperature and moisture), plastic characteristics and on microorganisms and their own optimal growth conditions in soil [13,15]. Biomedical polyolefins accumulates in the environment at a rate of millions tons per year. Biodegradation of medical polyolefins has become very important in the field of research for few decades. These polyolefins have been found to undergo radio and photo-induced biodegradation in accelerated composting conditions [11,12,16,17]. Recently, we have investigated the biodegradation of γ-sterilized biomedical polyolefins under composting and fungal culture environments [11,12]. The outcomes of our previous studies indicate that the pretreatment either by γ-sterilization [11,12] or by UV-irradiation [14,15] can enhance the biodegradation of polyolefins in biotic conditions. There have been no real discussion/report in the literature about the effect of different sterilization methods (high-energy radiation, photo-irradiation and heat sterilization processes) on the biodegradability of additive free biomedical PP under the same biotic and experimental conditions. In addition, study the effects of different sterilization methods on the biodegradability and the comparison of data from different researches are complicated by differences in biotic and experimental conditions. Thus, it will be worthwhile to study and to compare the effect of different sterilization methods on the biodegradation of biomedical PP under the same biotic and experimental conditions. The aim of the present work is to conduct a comparative study on the effect of different sterilization methods on the biodegradation of medical grade PP under the same biotic and experimental conditions. Three common sterilization techniques were applied: steam (121°C, 30 min), γ-irradiation (Co^{60}, 2.5 Mrad) and UV-irradiation (0.5 W cm^{-2}, ≤ 280 nm). The effect of these sterilization methods on the biodegradation of additive free polypropylene under the same composting and microbial culture environments was investigated.

Materials and Methods

Materials

The polypropylene pellets (Medical grade) were obtained from M/s. Indian Petrochemical Limited, Baroda, India, and purified by refluxing with xylene under nitrogen atmosphere, precipitated, filtered with cold methanol and dried at 50°C in vacuum oven. These samples were assumed to be 'additive free'.

Films preparation and sterilization

The purified samples were molded into 100 ± 10 μm thickness film in aluminum foil between two plates by heating at 210°C and holding for 1 min and then increasing the molding pressure to 15000 pounds. The pressure was allowed to fall, the mold were then immediately quenched into a large bath filled with water at 20°C. The films were sterilized under different sterilization methods; gamma sterilization, ultraviolet sterilization and autoclaving. The films were sterilized under γ-radiation at room temperature in presence of air (at dose 2.5 Mrad, ^{60}Co source, dose rate 0.81 Mrad h^{-1}). The γ-sterilized samples designated as "G-PP". While steam-sterilized samples (autoclaving by heating to 121°C for 30 min and 32 Psi) designated as "S-PP" and UV-irradiated films (0.5 W cm^{-2}, ≤ 280 nm) designated as "U-PP". Unsterilized films were designated as "neat" in this study.

Viscosity measurements

Intrinsic viscosities [η], were determined in decalin solution at 135°C. The antioxidant, 0.1 wt% (2, 6-di-tert-butyl-p-cresol) was added to prevent any further degradation. The decalin solution was filtered through a No.3 glass filter at 70°C before dissolving the PP films. The viscosity-average molecular weight (M_v) was calculated from the intrinsic viscosity by using Mark-Houwink equation: $[\eta] = K M^a$. The constant values K and a were taken from Reference [18]. The error due to expansion of flask is negligible as preheated flask and pipette (140°C) were used to mix the solvent into an Ubbelohde viscometer.

Incubation in compost

The biodegradability tests were performed in a laboratory scale composter, and the size of the films was 5 × 5 cm. The constitution [17,19] of solid waste mixture (compost) used for biodegradability testing of PP samples was as follows (dry weight): 40.8% shredded leaves, 11.4% cow manure/dung, 15.8% newspapers and computer paper, 2% white bread, 7.8% sawdust, 19.2% food waste (dry milk, potato, carrot, banana, and others vegetables) and 3.0% urea. After 3 months of maturation period at 30–40°C, the compost was used for testing. Small fragments of green grass covered the composting bin and the moisture content was maintained by periodically spraying of water. To avoid anaerobic conditions, the bin was constantly aerated with oxygen through a hollow tube. The samples were kept inside the compost at 3.5 feet depth. The weight loss of neat and sterilized composted samples was measured monthly during 7 months of composting by removing, washing the samples with distilled water and ethanol and drying in a vacuum oven at 60–65°C until constant weight. The biodegradability was determined by measuring the gravitational weight loss (per surface area in gm/cm^2) on digital balance, Prescisa 205 SCS, Switzerland. It was observed that the temperature of compost had been slightly higher than atmospheric temperature and the temperature of compost increased to approximately 43°C in 4 months and then began to drop (Figure 1).

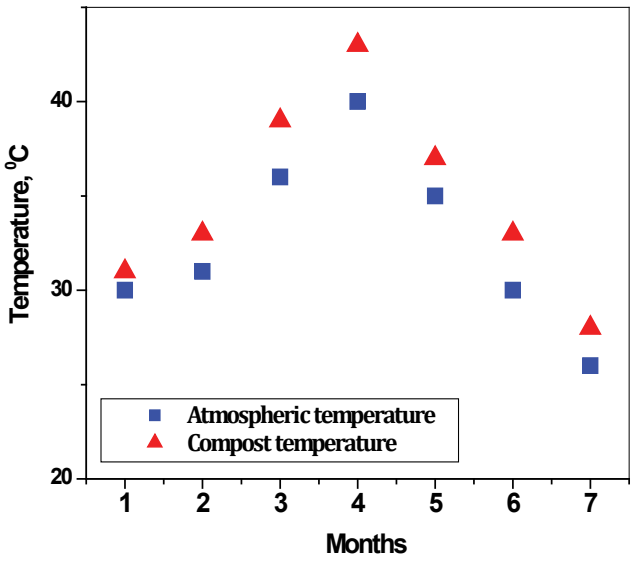

Figure 1: Temperature profile of composting.

Incubation in culture

The PP samples were used as the sole carbon source for a fungus, eg, *Aspergillus niger*. The samples were kept in the culture medium of *A. niger* as a sole carbon source for 7 weeks. The test fungi were cultivated by inoculating in Sabouraud Dextrose Agar (SDA) of pH 6.5 at 28°C for 4 days. The SD agar was prepared by dissolving 10 g of peptone, 40 g of dextrose, 15 g agar in one liter of deionized water. The basic salt agar for testing the fungal growth on polymer was prepared by dissolving potassium dihydrogen phosphate (0.70 g), magnesium sulfate (0.70 g), ammonium nitrate (1.0 g), sodium chloride (0.005 g), ferrous sulfate (0.002 g), manganese sulfate (0.001 g) and agar (15.00 g) in one liter of deionized water. After the medium was sterilized at 120 ± 5°C for 25 min, the pH was adjusted between 6.5 and 7.0 by addition of a 0.1 N solution of NaOH. For providing the solidified agar layer (depth 4-7 mm) basic salt agar was poured into sterilized petri dish. Since longer time is necessary for degradation by fungus, spores were sprayed in more quantities on the surface of neat and sterilized samples. The petri dishes were incubated at 28-30°C after sealed by wax to avoid the contamination for seven weeks. The rate of fungal growth was estimated with naked eyes in accordance to ASTM G-2170 where the recorded parameter (S) is the fraction of the surface covered by fungus ($S < 10\%$ (1), $10 \leq S < 30\%$ (2), $30 \leq S < 60$ (3) and $S \geq 60\%$ (4)).

FT-IR spectroscopy

FT-IR (Fourier transform infrared 16 PC spectrometer) was used to characterize the chemical changes in the polymer films, and our interest was mainly focused on the carbonyl region (1600-1800 cm^{-1}) to compare the oxidation due to the different sterilization methods [20,21]. The carbonyl index of the samples was determined from the ratio of the areas of the absorbance bands in the ranges of 1850–1654 cm^{-1} region to the range of 2750–2694 cm^{-1}.

Scanning electron microscopy

The films were placed in stoppered bottles containing osmium tetroxide (2% aqueous) and allowed to stand for 48 h. The films were washed with water and dry ethanol and they were dried under vacuum for 24 h at 50°C. The gold-coated samples were examined under electron microscope (Leica Cambridge Stereoscan 440 model).

Mechanical properties

A universal testing machine, Instron Model 4201, measured the changes in the tensile properties. Elongation at break was determined from stress-strain curves. The cross speed used was 10 mm min^{-1}. The specimens used were 100 mm length, 10 mm width and the gauge space 50 mm. The results of each sample were taken as the average of five specimens.

Results and Discussion

FTIR spectral changes

Figure 2 shows the FTIR spectral changes (the carbonyl region at 1600-1800 cm^{-1}) of PP films before and after sterilization under different sterilization methods. The presence of carbonyl groups detected as absorption peaks in the range of 1690-1760 cm^{-1} is evidence of oxidative degradation degree [22]. The major band at 1720 cm^{-1}, regularly used to monitor the oxidation process, is attributed to ketones. An increase in absorbance at the carbonyl region was observed for all sterilized samples. The increase in absorption can be attributed to the radio, photo, and thermal oxidative degradation initiated during sterilization processes. Throughout the course of sterilization, the carbonyl region displays the presence of γ-lactones at 1785 cm^{-1}, carboxylic acids at 1712 cm^{-1}, ester at 1740 cm^{-1}, peracids at 1750 cm^{-1} and peresters at 1777 cm^{-1} and a shoulder at 1685 cm^{-1} assigned to α, β-unsaturated ketones (-CH=CH-CO-). The formation of oxidation products in γ-sterilized samples (G-PP) was higher than UV-irradiated samples (U-PP), while steam-sterilized samples (S-PP) showed lower oxidation products. This indicates that the oxidative degradation occurred due to γ-sterilization is higher than other sterilization methods. The effect of various sterilization methods on the degree of oxidation of PP was apparent. FTIR spectral changes clearly demonstrate that the degree of oxidation which occurred during sterilization mainly depends on the utilize sterilization method.

Variation in viscosity

Table 1 shows the changes in intrinsic viscosities [η] of PP films before and after sterilization. It was observed that the intrinsic viscosity

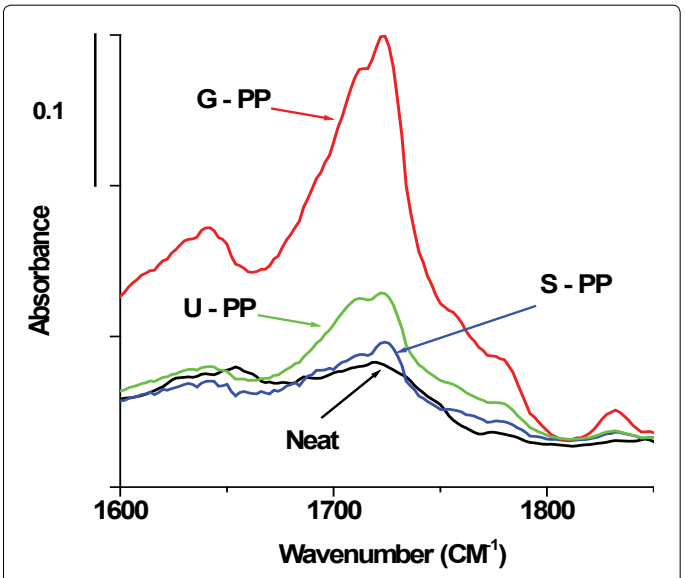

Figure 2: FT-IR spectra (carbonyl region) before and after sterilization; unsterilized (neat), γ-sterilized (G-PP), UV-irradiated (U-PP) and steam-sterilized (S-PP) samples.

Samples	Neat	S-PP	U-PP	G-PP
Intrinsic viscosity	1.85	1.76	1.32	0.86

Table 1: Changes in intrinsic viscosity [η] after sterilization; unsterilized (neat), γ-sterilized (G-PP), UV-irradiated (U-PP) and steam-sterilized (S-PP) samples.

of G-PP drastically reduced, while S-PP slightly decreased. Among all the sterilized samples, the decrease in intrinsic viscosity was observed to be lower for S-PP samples. The decrease in [η] can be attributed to the chain scission or the formation of low molecular weight compounds during sterilization. It seems that the PP samples undergo higher rate of chain scission under γ-sterilization compare to other sterilization methods. Conversely, S-PP samples have shown lesser chain scission. Among the radiation-sterilized samples, UV-irradiated samples have shown lower chain scission. These results supported to that obtained from FT-IR where the concentration of the oxidation products were found to be higher for G-PP and lower for S-PP, indicating that the γ-sterilization process is more damaging that than UV and steam processes.

Mechanical properties

The effect of different sterilization methods on mechanical properties in terms of elongation at break (%) can be seen in Figure 3. After sterilization, the decrease in the values of elongation at break (%) was observed for all sterilized samples. As expected, the elongation at break varies with changing the method of sterilization. Among all sterilized samples, S-PP samples have shown very less/marginal decrease in the value of elongation at break. Conversely, the elongation at break drops massively for γ-sterilized samples. In comparison of all sterilized samples, the G-PP samples have shown higher degradation and become liable to embrittlement. Generally, the elongation at break is a parameter to monitor the radio and photo-oxidation of polymers as it is very sensitive to the molecular and morphological changes undergone by the polymer during irradiation [23-25]. The results of mechanical properties indicate that drops of elongation at break correspond well to the results obtained by FTIR characterization and the viscometric measurements. The changes in the rate of oxidation and intrinsic viscosity of G-PP/U-PP/S-PP are supplementary supported by a similar trend detected in the changes of elongation at break. These results demonstrated that the reduction in elongation at break (%) is attributed to the chain scission in polymer backbone which occurred during sterilization. Accordingly, radiation sterilization techniques (esp. gamma irradiation) have the most severe effect on polypropylene material. However, steam sterilization hardly affects the polymer matrix.

Morphological changes

SEM is a significant and reliable tool to show the morphological changes of degraded polymer. Figure 4 presents the changes in surface morphology after sterilization with different methods in comparison with unsterilized sample. Based on these micrographs it can be seen that the PP samples showed smooth surface before sterilization (Figure 4a). On the other hand, all sterilized samples exhibited cracked/deformed surfaces. These transformations are perhaps related to oxidation occurring on the surface of the polymer films within the thickness of a few microns during sterilization. The visualization of the images representing the surface morphology of the sterilized samples provided evidence that a substantial difference occurred in the surface morphology due to changing the methods of sterilization. SEM results showed deep erosion on the surface after γ-sterilization (Figure 4b). The cracks formation on the surface of UV-irradiated samples is lesser (Figure 4c) than γ-sterilized samples while steam-sterilized samples (Figure 4d) have shown mostly smooth surface. It is evident from the micrographs that both radiation sterilization processes causes eroded/cracked surface. The higher surface deterioration observed in both radiation-sterilized samples confirm the results of elongation at break (%). As it is seen that the decrease in elongation at break can also be attributed to the crack formation on the surface. Since eroded surface or cracks on the surface can act as "defects" where failure mechanism is initiated [26]. The cracked surface accelerates the degradation further because the oxidative degradation is initiated at surface only. This study revealed that radiation-sterilization (gamma and UV irradiation) produced more detrimental processes in contrast to steam sterilization process. It can be inferred from the results of FTIR, viscosity, mechanical properties and SEM that, the increasing order in the rate of degradation due to using different sterilization techniques as follows; G-PP > U-PP > S-PP.

Composting

Weight loss is one of the most valuable data indicating the actual biodegradation of polymeric material after composting whenever

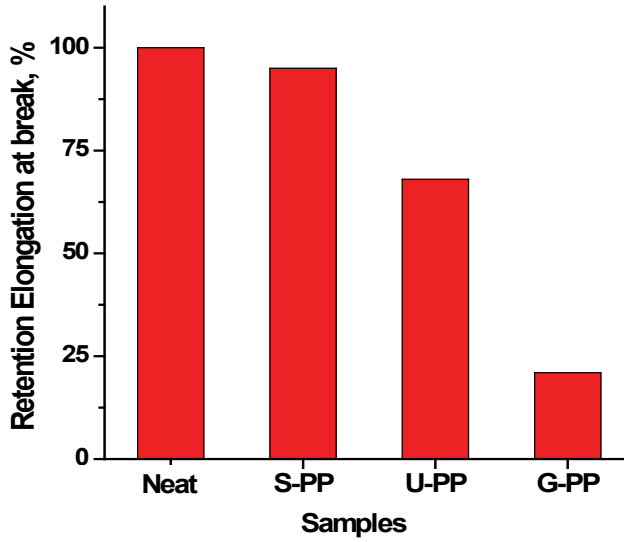

Figure 3: Effect of different sterilization techniques on mechanical properties; unsterilized (neat), γ-sterilized (G-PP), UV-irradiated (U-PP) and steam-sterilized (S-PP) samples.

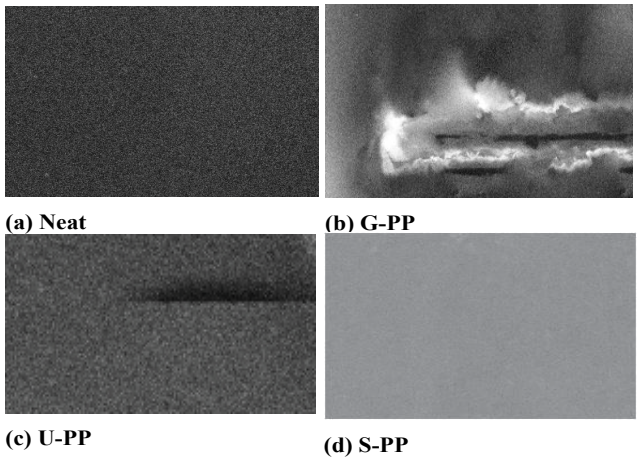

Figure 4: SEM of unsterilized (neat), γ-sterilized (G-PP), UV-irradiated (U-PP) and steam-sterilized (S-PP) samples.

validated by parallel monitoring of the neat respirometric microbial activity bound to the carbon content of the sample under testing. Figure 5 represents the weight loss of neat and sterilized samples during 7 months of composting. It was observed that the degradation rate increased with increasing the time of incubation in compost. It is evident from Figure 5 that the biodegradation rate significantly depends on the nature of utilized sterilization method. Amongst all the sterilized PP samples, the G-PP samples showed higher rate of weight loss, while S-PP samples have shown lower weight loss. The U-PP showed lower weight loss than that in G-PP samples. The weight loss of S-PP was slightly higher than unsterilized samples and more stable towards the microbial attack than other sterilized samples. The 5 months composted, G-PP samples were not recoverable from the compost, while UV-sterilized sample also did not show recoverable behavior from the compost after 7 months suggesting the biodisintegration of films in composting and the acceleration of biodegradation process due to changing the method of sterilization. In Figure 1, temperature of compost was found to be higher than atmospheric temperature. This may be due to the fact that in the earlier months of composting, compost itself could increase the temperature because of exothermic microbial degradation [20,27,28]. In correlation of Figures 1 and 5, it can be seen that the weight loss was lower for initial days and rapidly increases after 3-4 months suggesting that temperature of compost will have a significant effect on the biodegradation. During the observation of unsterilized and sterilized samples, after 4 months of composting, weight loss (%) was 13% for unsterilized whereas S-PP, U-PP and G-PP sterilized samples respectively showed 19, 38 and 74% weight loss. Weight loss test demonstrated that the biodegradability of PP under the same biotic conditions mainly depend on the nature of sterilization method (heat, photo, and high-energy radiation). It is evident that that the radio and photo-degradation can enhance the degradability of PP in biotic environment.

Incubation in culture

The visual growth rating [29] test is valuable in assessing the performance of polymer during its use under such conditions. The samples were kept in the culture medium of *Aspergillus niger* as a sole carbon source for 7 weeks and biodegradation characteristics were compared with those in composting. During incubation with fungal culture, the spores (black spots) as colonies were observed to grow. Table 2 represents the data of fungal colonization (visual growth) on the surface of polymer films during 7 weeks of incubation in culture. The absence of any colonization in a controlled petri-dish (without polymer sample) clearly suggests that fungus is using the polymer specimen as a sole source of carbon, as there was complete absence of carbon in nutrient agar. Sterilized samples have shown higher fungal colonization than unsterilized and it was increased with increasing the time of incubation. The microbial growth was observed in the unsterilized sample after 7 weeks, while it was seen for γ-sterilized samples after 1 week. Fungal coverage was markedly affected by the method of sterilization. In comparison of sterilized samples, the coverage on the surface of films was much more for γ-sterilized films and lower on the surface of steam-sterilized films. In case of radiation-sterilized samples, fungal colonization was lower on the surface of U-PP than that of G-PP. It was interesting to observe that among all incubated samples, the fungal colonization was much more on the surface of radiation-sterilized samples (G-PP and U-PP). The higher colonization on radiation-sterilized films can be attributed to easy consumption of short chains as energy source by fungus. The more degradation (visual colonization) was same during composting, indicates that the functional groups have been generated during radio and photo-oxidation, and therefore, are initially responsible for the consumption of films by *A. niger*.

Variations in viscosity

The variations in intrinsic viscosity [η] of neat and sterilized samples during composting are tabulated in Table 3. During composting, with increasing time of incubation, the gradual decrease in intrinsic viscosity was observed for both sterilized and unsterilized samples. It was clearly seen that γ-sterilized samples showed lower [η] than that sterilized with UV irradiation and steam. Under composting, chain scission was observed to be lower at initial days of composting and to increase with increasing time of incubation as well as with increasing the compost temperature (Figure 1). Chain scission under composting condition also was observed to be higher but less than that observed after sterilization. The variations in the rate of intrinsic viscosity and weight loss during the incubation time seems to be similar but with opposite trend. This reveals that the biodegradation process is accompanied by chain scission/reduction in molecular weight thereafter weight losses. This may be due to the microbial consumption of low molecular weight (functional group) compounds present at the polymer backbone chain.

FTIR spectral changes

During the period of composting, the microorganisms utilize the carbonyl residues and reduce their concentration. Therefore, it

Samples	Weeks						
	1	2	3	4	5	6	7
Neat	0	0	0	0	0	0	1
S-PP	0	0	0	0	0	1	2
U-PP	0	0	0	1	2	3	3
G-PP	0	1	2	3	3	4	4

Table 2: Visual growth rating of *Aspergillus niger* on the surface of neat and sterilized films during 7 weeks of incubation in culture.

Composted Sample	Incubation time (Months)							
	0	1	2	3	4	5	6	7
Neat	1.85	1.82	1.75	1.63	1.47	1.32	1.15	1.02
S-PP	1.76	1.73	1.65	1.52	1.35	1.14	0.95	0.81
U-PP	1.32	1.26	1.15	0.95	0.75	0.53	0.34	0.21
G-PP	0.86	0.77	0.63	0.44	0.25	–	–	–

Table 3: The variations in intrinsic viscosity [η] of the composted neat and sterilized samples during 7 months.

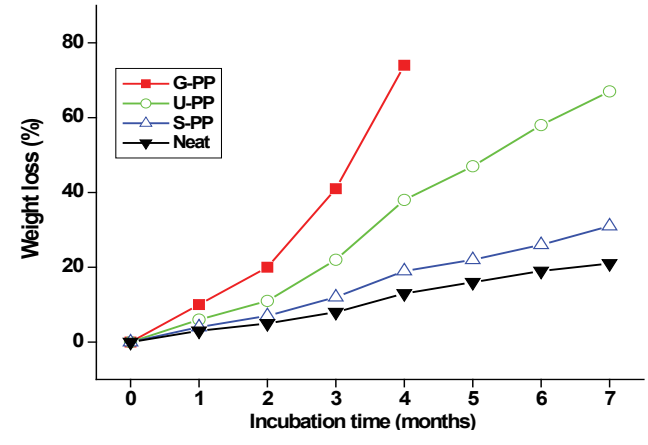

Figure 5: Weight loss (%) of unsterilized (neat), γ-sterilized (G-PP), UV-irradiated (U-PP) and steam-sterilized (S-PP) samples.

important to monitor the biodegradability of polymer by measuring the concentration of carbonyls groups during the period of composting. The FT-IR spectral changes after composting of sterilized samples have shown a decrease in carbonyl region (esp. G-PP and U-PP). The reduction in carbonyl residues was estimated in terms of a carbonyl index (Table 4). It was found that the composting of gamma and UV sterilized samples reduce the carbonyl index. This it may be due to the release of short chain carboxylic acids in the form of degradation products during the biotic step [27,28,30,31]. This decrease was not much significant, since there may be incomplete consumption of carbonyl compounds and may be possibility of continuing oxidation processes (thermal oxidation and aerobic condition). In contrast to S-PP, U-PP and G-PP showed higher reduction in the concentration of carbonyl groups during the period of composting.

Morphological aspects

Figure 6 display the scanning electron micrographs of composted samples before and after sterilization. In comparison to sterilized films (before composting), many cavities and cracks were observed in the composted films, probably caused due to the microbial attack, suggesting that microorganisms penetrate the polymer matrix during the degradation process. The cavities on the surface were observed after composting of all samples. The presence of small and large cavities on the surface may be due to the absence of a uniform distribution of short branches or degradation products generated during sterilization, which are preferable carbon source (food) for microorganisms. Their consumption by microbes results in good erosion on the surface of polymer films. The erosion on the surface of radiation-sterilized samples (G-PP and U-PP) was evidently seen (Figure 6b and 6c). However, little erosion on the surface of steam-sterilized and neat samples was observed (Figure 6a and 6d). The deformation/deepness of erosion on the surface of G-PP samples was high, which may be due to the higher extent of oxidation in comparison with UV-sterilized samples (U-PP). Observably, the macro-cracks (that resulted from gamma and UV degradation) acted as initial point of attack by microorganisms, providing food material and accessibility to the microbial cells to slowly degrade the PP films during composting. It is well known that during radio and photo-oxidative degradation, the polymer chains undergo chain scission and the surface is the place where the initiation of degradation process takes place (Figure 4). It is obvious that the crack formation (amorphous) on the surface may accelerate considerably the rate of biodegradation since any kind of degradation (photo or radio oxidation) is initiated at the amorphous surface of the polymer samples. The radiation oxidative-degradation process occurs initially and dominantly on the surface of the films causing cracks/erosion and then it moves into polymer matrix by penetration of microorganisms (during composting), which finally enhance the rate of biodegradation. Thus, the G-PP and U-PP composted samples showed remarkable eroded/cracked/deformed surfaces. It is evident that the biodegradation of polypropylene was enhanced by oxidation pretreatment (radio/photo-oxidation), which increases surface hydrophilicity by the formation of carbonyl/oxidation groups that can be utilized by microorganisms. The results demonstrated that the biodegradability of PP under the same biotic conditions strongly affected by changing the method of sterilization.

Finally, it can be summarized that γ-sterilization causes severe degradation than UV irradiation in term of oxidation products, molecular weight, morphological changes, and mechanical properties. However, steam sterilization hardly affects the polymer matrix. In contrast to the composted steam-sterilized samples, the composted radiation-oxidized samples (esp. γ-sterilized samples) showed a marked reduction in the amount of molecular weight, carbonyl residues and higher weight losses and deep surface erosion. These results demonstrated that the radiation-oxidative pretreatment evidently enhance the biodegradation of biomedical PP while no noticeable effect was found on the biodegradability with the pretreatment of steam sterilization. Maximal biodegradation was obtained in combination with radiation sterilization techniques (esp. gamma sterilization). These results support our previous findings that the pretreatment either by γ-sterilization [11,12] or UV-irradiation [14,15] can enhance the biodegradation of polyolefins in biotic conditions. The increasing order in the rate of biodegradation was found to be similar to the increasing order in the rate of degradation after sterilization (G-PP > U-PP > S-PP). This indicates that the biodegradation rate at the same biotic conditions mainly depends on the rate of degradation that initially occurred during sterilization. This study revealed a clear relationship between the biodegradation and sterilization degradation. The higher surface deterioration and the increase in weight loss and the decrease in intrinsic viscosity and oxidation products of sterilized samples (esp. radiation-sterilized samples) after composting are evident that the degradation process occurs initially and dominantly on the surface of the films and then it moves into polymer matrix by penetration of microorganisms, which finally enhance the rate of biodegradation. This suggests that the chain scission, surface cracks and oxidized functional groups were important units in the bio-/degradation of polypropylene. By comparing the biodegradation rates of PP samples before and after sterilization with different techniques it can be conclude that the biodegradability of PP under the same biotic conditions significantly affected by changing the method of sterilization. After 4 months of composting in the same biotic conditions it was found that the pretreatment of γ-sterilization increases the rate of biodegradation 6 time compared to the unsterilized PP samples, while the photo-oxidative pretreatment increased it 3 time. The results of this study may contribute in solving the environmental problem of medical disposables, which accumulated in the environment at a rate of millions tons per year.

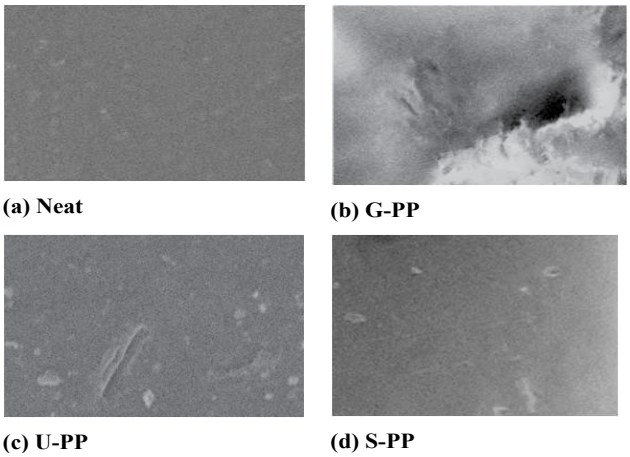

Figure 6: SEM of composted samples; unsterilized (neat), γ-sterilized (G-PP), UV-irradiated (U-PP) and steam-sterilized (S-PP) samples.

Samples	After sterilization	After composting	
		2 months	4 months
S-PP	0.09	0.09	0.07
U-PP	0.23	0.21	0.17
G-PP	0.47	0.38	0.21

Table 4: Carbonyl indices obtained from FTIR spectra of sterilized samples before and after composting.

Conclusion

The main objective of this work was to conduct a comparative study on the effect of different sterilization methods (gamma, UV and steam sterilization) on the biodegradation of biomedical polypropylene under the same biotic and experimental conditions. Radiation-sterilized samples (esp. γ-sterilized samples) were found to be more susceptible to biodegradation than steam-sterilized samples. It was found that the biodegradation rate of sterilized polypropylene basically depend on the rate of degradation that initially occurred during sterilization, where the chain scission, surface cracks and oxidized functional groups formed by photo and radio-oxidation play an important role in the bio-/degradation. Our findings clearly established that the polypropylene undergoes photo and radio-induced biodegradation in accelerated composting conditions. We conclude from this investigation that the biodegradation of sterilized PP under the same biotic conditions mainly depends on the nature of sterilization (i.e., on the rate and the type of degradation that initially occurred during sterilization). In addition, the pretreatment of sterilization using severe process (such as γ-sterilization) can significantly accelerate the biodegradation of biomedical PP matrix in biotic conditions considerably. The biodegradability of the medical disposables wastes may effectively accelerated through proper pretreatment method and suitable biotic conditions.

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