

Synthesis and Characterization of Polyethylene Modified Through Phase-Transfer-Catalyzed Graft Copolymerization

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ABSTRACT: In an effort to impart biodegradability, polyethylene (PE) was modified through the graft copolymerization of vinyl monomers such as acrylamide (AAM) and acrylic acid (AAc) by a phase-transfer-catalyst method. The grafting percentage of AAM and AAc for PE was found to be dependent on the dibenzoyl peroxide concentration, monomer concentration, time, temperature, and concentration of the phase-transfer catalyst. Some AAM- and AAc-grafted PE samples were prepared by chemical, UV, and γ -radiation methods. The biodegradation of samples of PE, polyethylene-g-poly-

acrylamide, and polyethylene-g-poly(acrylic acid) prepared by all these methods was studied. The weight loss of the samples over a period of time was observed with soil-burial tests. The grafted samples prepared by the phase-transfer-catalyst method showed better biodegradation results than those prepared by other methods of grafting. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 140–147, 2008

Key words: biodegradable; FTIR; graft copolymers; phase transfer catalysis; polyethylene (PE)

INTRODUCTION

The modification of polymers by graft copolymerization can add many properties to the trunk polymers. Numerous methods have been suggested for the preparation of graft copolymers, including chemical and radiation techniques. The common feature of most methods is that the active site is created in a pre-existing macromolecule. A graft copolymer is then obtained from this activated polymer through the polymerization of an appropriate monomer. The use of a phase-transfer catalyst (PTC) for carrying out the polymerization reaction is a new method used recently for the polymerization of some monomers. Using several ammonium and phosphonium salts as PTCs, Tagle et al.¹ carried out the polymerization of 2,2-bis(1,4-phenyleneoxy)propylidene diacetic acid and related acids with diphenols. Using benzyltributylammonium chloride as a PTC and potassium peroxydisulfate as an initiator at a constant temperature (60°C) in an inert atmosphere under unstirred conditions, Umapathy et al.² studied the kinetics of the free-radical polymerization of methylacrylate. Tagle et al.³ derived polycarbonates

and polythiocarbonates from diphenols containing Si or Ge [bis(4-hydroxyphenyl)dimethylgermane, bis(4-hydroxyphenyl)diphenylgermane, bis(4-hydroxyphenyl)dimethylsilane, and bis(4-hydroxyphenyl)diphenylsilane], and phosgene and thiophosgene were synthesized under phase-transfer conditions with several PTCs. Seno et al.⁴ prepared vinyl phenylsulfonacetate through the reaction of vinyl chloroacetate with sodium benzenesulfinate in acetone in the presence of a PTC. The polymerization of vinyl phenylsulfonacetate with 2,2'-azobisisobutyrate was kinetically investigated in acetone. Graft copolymerization using PTCs has not been explored. In our laboratory, we have studied the polymerization of a water-soluble monomer, acrylamide (AAM), with a water-insoluble initiator, dibenzoyl peroxide (BPO), and its grafting onto a water-insoluble polymer backbone (isotactic polypropylene) by a PTC method.⁵

Although the benefits conferred on society by the development of manmade polymers are enormous, in recent years, the problem of their ultimate disposal, their significant effect on environmental pollution, and their potential danger to wildlife have been noted.⁶ Most polymers are resistant to attacks by microorganisms. Any attempt to modify such polymers by the introduction of functionalities that are labile to microbial attack would be beneficial. Therefore, the term *biodegradation* in recent years has become a part of a green vocabulary. Akmal et al.⁷ carried out the microbial biodegradation of polyester

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poly(3-hydroxybutyrate) and its copolymer poly(3-hydroxyvalerate) through a soil-burial test and observed different rates of degradation. Synergistic effects from combining UV/sunlight and a soil-burial treatment on the biodegradation rate of low-density polyethylene/starch blends were studied by El Rehim et al.⁸ Blends of polypropylene and starch-based biodegradable materials were tested for biodegradability by Ramis et al.⁹ under the conditions of a soil-burial test. The biodegradation of γ -sterilized biomedical polyolefins under composting and fungal culture environments was studied by Alariqi et al.¹⁰

In this study, therefore, an attempt was made to graft-copolymerize AAm and acrylic acid (AAc) onto polyethylene (PE) with tetrabutyl ammonium bromide as a PTC. To determine the effect of the introduction of functionalities such as $-\text{COOH}$ and $-\text{CONH}_2$ on the degradability, biodegradation studies of PE and grafted PE with soil-burial tests were carried. Different samples of polyethylene-*g*-polyacrylamide [PE-*g*-poly(AAm)], prepared by photochemical-induced, chemical-induced, and γ -radiation-induced graft polymerizations, were also subjected to soil-burial tests. The weight loss was noted after regular time intervals.

EXPERIMENTAL

Material and methods

Commercial PE in the form of beads was dissolved in *p*-xylene by heating and filtered. The filtrate was precipitated by the addition of methanol. The mixture was filtered again. The residue was washed, dried, and crushed to a fine powder. Benzoyl peroxide (S.D. Fine Chemicals, Mumbai, India) was used as a free-radical initiator, and *p*-xylene (Merck, München, Germany) was used as a solvent for AAm and AAc. Methanol (S.D. Fine Chemicals) was used as a nonsolvent. AAm (Merck) was dried before use. AAc (S.D. Fine Chemicals) was distilled before use. Tetrabutyl ammonium bromide (Merck) was used as received.

Graft copolymerization

A definite amount (100 mg) of recrystallized PE was dissolved in a definite amount of *p*-xylene (10 mL) in a reaction flask. To it was added a definite amount of AAm (0.5×10^{-2} to 3.5×10^{-2} mol)/AAc (1.46×10^{-2} to 5.09×10^{-2} mol) dissolved in a known volume of water (10 mL). A definite amount of a PTC (tetrabutyl ammonium bromide; 1×10^{-2} to 3.4×10^{-2} mol) was added to the reaction mixture. The reaction flask was placed in a water bath at a constant temperature (30–80°C) under constant stirring for a definite period of time (60–180 min). After the stipu-

lated time, methanol was added to the reaction mixture to precipitate the grafted copolymer, homopolymer, and unreacted backbone polymer (PE). The reaction mixture was filtered and washed thoroughly with hot water to remove the homopolymer. The grafted PE was dried at 45°C and weighed until a constant weight was obtained. The percentage of grafting (P_g) was calculated as follows:

$$P_g = (W_2 - W_1)/W_1 \times 100$$

where W_1 and W_2 are the weights of pristine PE and grafted PE, that is, PE-*g*-poly(AAm), PE-*g*-poly(AAc) after the complete removal of the homopolymer, respectively.

Characterization of the graft copolymer

IR spectroscopy and thermogravimetric analysis (TGA) methods were used to characterize the graft copolymer.

Role of the PTC

To ascertain that the graft copolymerization occurs via a phase-transfer mechanism, some reactions were carried out in the absence of a PTC with a unitary solvent system, that is, water or xylene alone, or a binary system, that is, a mixture of water and xylene, or with a PTC in a unitary solvent system of either H₂O or xylene. The following reactions were performed:

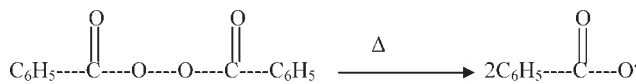
1. Without a PTC with BPO in water (PE = 100 mg, AAm = 100 mg, BPO = 100 mg, H₂O = 20 mL).
2. Without a PTC with BPO in *p*-xylene (PE = 100 mg, AAm = 100 mg, BPO = 100 mg, xylene = 20 mL).
3. Without a PTC with BPO in 1 : 1 (v/v) H₂O/*p*-xylene [PE = 100 mg, AAm = 100 mg, BPO = 100 mg, H₂O/xylene = 10 : 10 (mL)]
4. With a PTC with BPO in *p*-xylene (PE = 100 mg, AAm = 100 mg, BPO = 100 mg, *p*-xylene = 20 mL, PTC = 100 mg).
5. With a PTC with BPO in H₂O (PE = 100 mg, AAm = 100 mg, BPO = 100 mg, H₂O = 20 mL, PTC = 100 mg).

In all cases, the reaction mixture was stirred for 2 h at 60°C. The addition of methanol precipitated PE and AAm, which were found to dissolve in *p*-xylene and water, respectively. No graft copolymer could be separated.

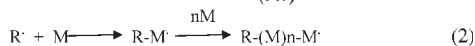
These observations support the fact that the graft copolymerization reactions proceeded via the phase-transfer mechanism.

RESULTS AND DISCUSSION

BPO is a known free-radical initiator used to carry out the polymerizations of various vinyl monomers and graft copolymerization reactions. The general mechanism of the initiating ability of BPO is well known and involves the following steps:

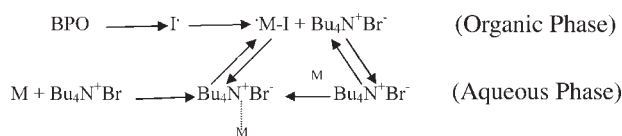


The phenyl radical ($\text{R}\cdot$) has the ability to abstract hydrogen atoms from the polymeric backbone (PE in this case) to initiate the copolymerization reaction. The initiation of the monomer is also facilitated by the phenyl radical. The reactions can be predicted as follows:



where $\text{R}\cdot$ is a radical species generated from BPO. Because the reaction is being carried out in a two-phase system, reaction 1 takes place in the organic phase, and reaction 2 occurs after the transport of the monomer in the aqueous phase to the organic phase, in which it comes into contact with the radical $\text{R}\cdot$ or with the macroradical $\text{PE}\cdot$.

The interaction of the reactants, that is, the PE, monomer, and initiator, distributed between the two phases, that is, the organic and aqueous phases, is due to the presence of a PTC, that is, $\text{Bu}_4\text{N}^+\text{Br}^-$. The transfer of the reactants from the aqueous phase to the organic phase by the PTC can be visualized as follows. For the PTC mechanism for the polymerization of monomers,



For the PTC mechanism for the graft copolymerization of monomers onto PE,

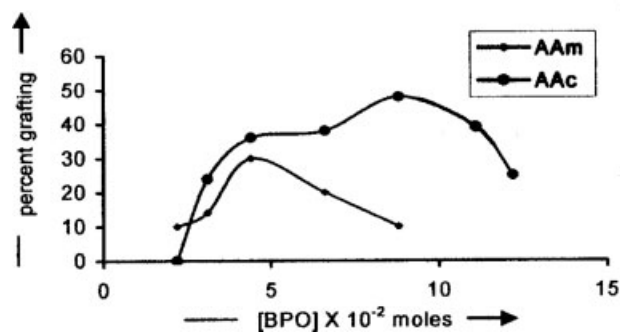
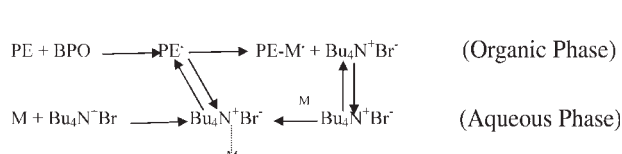
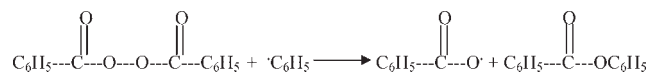


Figure 1 Effect of the variation of the BPO concentration on P_g of AAm and AAc for PE.

PE and BPO, being soluble in *p*-xylene, are present in the organic phase (xylene). BPO generates the initiating radicals, which activate the PE backbone by abstracting hydrogen and thus offering active sites at which grafting takes place. The monomers (AAm and AAc), being soluble in water, are present in the aqueous phase. The PTC is soluble in both the organic and aqueous phases, so it transports the water-soluble monomer to the organic layer. The initiation of the monomer in the organic phase takes place by the initiator radical and by the PE macroradical in the organic layer. The monomer free radical terminates either to produce the graft copolymer or to form the homopolymer. The copolymerization of AAm and AAc onto PE has been studied as a function of different reaction parameters, such as the initiator concentration, monomer concentration, PTC concentration, time, and temperature, and the results are explained in the light of this proposed mechanism.

Effect of the BPO concentration

The graft copolymerization of AAm and AAc onto PE was studied as a function of the BPO concentration, and the results are represented in Figure 1. P_g of AAm and AAc for PE increased with an increase in the BPO concentration, having maximum values of 30 and 48% at the BPO concentrations of 4.4×10^{-2} and 8.8×10^{-2} mol, respectively. A further increase in the concentration of BPO beyond the optimum value reduced P_g . This may have been due to the fact that at higher concentrations, BPO underwent induced decomposition, which led to a decrease in the radical concentration and hence lowered the graft copolymer formation:



Also, at a higher BPO concentration, more homopolymer was formed at the expense of the graft copolymer.

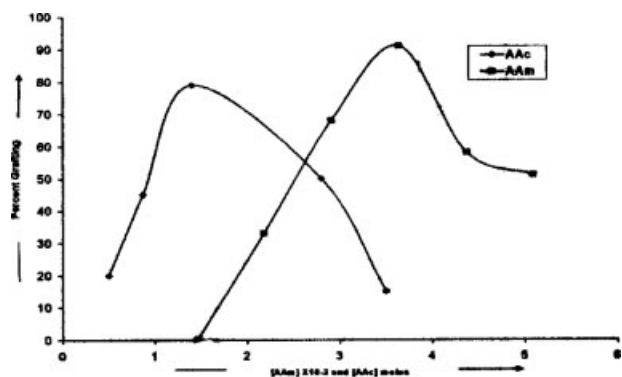


Figure 2 Effect of the variation of the monomer concentration on P_g of AAm and AAc for PE.

Effect of the monomer concentration

P_g of AAm and AAc for PE was studied as a function of the monomer concentration, and the results are presented in Figure 2. The maximum P_g value of AAm onto PE (79%) was obtained at an AAm concentration of 1.4×10^{-2} mol, beyond which it decreased. The decrease in P_g at a higher monomer concentration was due to preferential homopolymer formation in comparison with grafting. The higher propagation rate (18,000 L/mol/s) and higher termination rate (14.5×10^6 L/mol/s) of AAm led to preferential homopolymerization rather than grafting. The decrease in P_g at a higher monomer concentration may also have been due to wastage of the monomer in chain-transfer reactions. The monomer-transfer constant and solvent-transfer constant for AAm were 0.6×10^{-4} and 0.204×10^{-4} ,⁸ respectively. P_g of AAc increased sharply with an increasing AAc concentration, having a maximum (91%) at an AAc concentration of 3.64×10^{-2} mol, beyond which it decreased. At a higher monomer concentration, homopolymer formation became the preferred process. Both homopolymers, that is, polyacrylamide [poly(AAm)] and poly(acrylic acid) [poly(AAc)], being soluble in water, increased the viscosity of the aqueous medium, which restricted the movement of the reactants in the aqueous phase and the transportation from the aqueous phase to the organic phase, leading to a decrease in P_g .

Effect of the PTC concentration

The effect of the PTC (i.e., $\text{Bu}_4\text{N}^+\text{Br}^-$) concentration on the P_g values of AAm and AAc for PE was studied, and the results are presented in Figure 3. There was an increase in the P_g values of AAm and AAc with an increasing PTC concentration. The maximum P_g values (50 and 68%) of AAm and AAc were obtained at PTC concentrations of 3.1×10^{-2} and 2.4×10^{-2} mol, respectively. Further increases in the

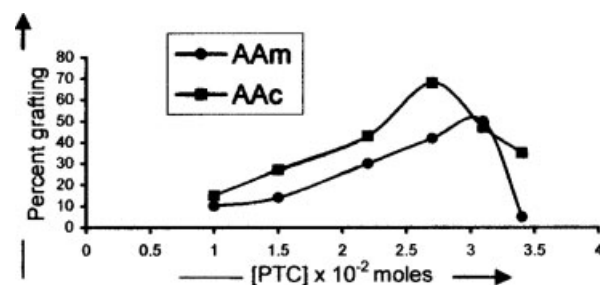


Figure 3 Effect of the variation of the PTC concentration on P_g of AAm and AAc for PE.

concentration of the PTC for both monomers led to a decrease in P_g . The initial increase in P_g of AAm and AAc with an increasing PTC concentration was due to the fact that the catalyst helped in transporting the monomer from the aqueous phase to the organic phase. An increase in the PTC concentration beyond the optimum further increased the transportation of the monomer to the organic phase, which may have led to more homopolymer formation. Both homopolymers [poly(AAm) and poly(AAc)], being soluble in water, increased the viscosity of the medium, leading to a decrease in P_g .

Effect of time

Figure 4 presents plots of P_g of AAm and AAc for PE as a function of time. P_g increased with an increase in the reaction time, with maximum grafting of 79% for AAm and 91% for AAc within 120 min, and decreased thereafter. The decrease in grafting may have been due to induced decomposition of the initiator and mutual annihilation of the growing polymeric chains, which led to preferential homopolymer formation.

Effect of temperature

The effect of temperature on P_g of AAm and AAc for PE was studied, and the results are presented in Figure 5. P_g increased with an increase in the

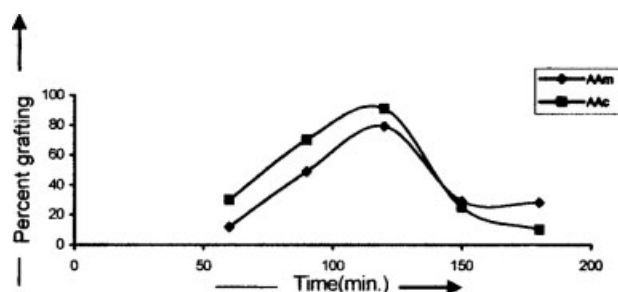


Figure 4 Effect of the variation of time on P_g of AAm and AAc for PE.

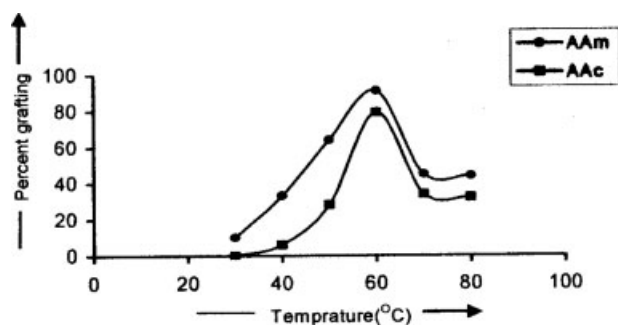


Figure 5 Effect of the variation of temperature on P_g of AAm and AAc for PE.

temperature, with maxima of 79 and 91% for AAm and AAc, respectively, at 60°C. A further increase in the temperature reduced P_g . The increase in P_g with increasing temperature was due to an increase in the decomposition of the initiator, which led to the formation of more free radicals and the generation of active sites on the polymeric backbone. The transportation to the monomer from the aqueous phase was also accelerated at a higher temperature, which led to a higher P_g value. A decrease in P_g beyond the optimum temperature was attributed to premature termination of the growing polymeric chains and to the occurrence of chain transfer and other wastage reactions.

Evidence of grafting

The evidence in favor of the formation of the grafts, PE-g-poly(AAm) and PE-g-poly(AAc), was based on IR spectroscopy and TGA.

IR spectroscopy

A comparison of the IR spectra of PE, PE-g-poly(AAm), and PE-g-poly(AAc) (Figs. 6–8) shows that

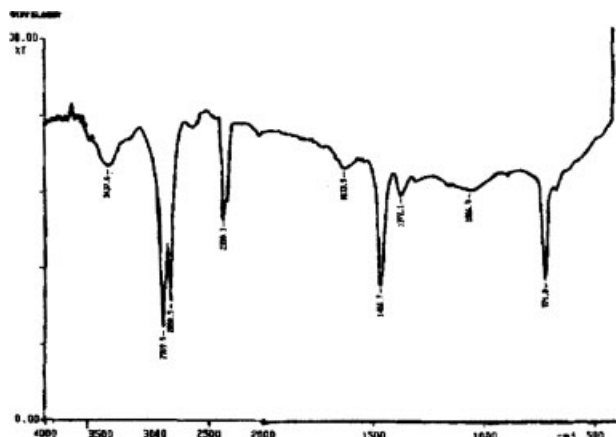


Figure 6 FTIR of PE.

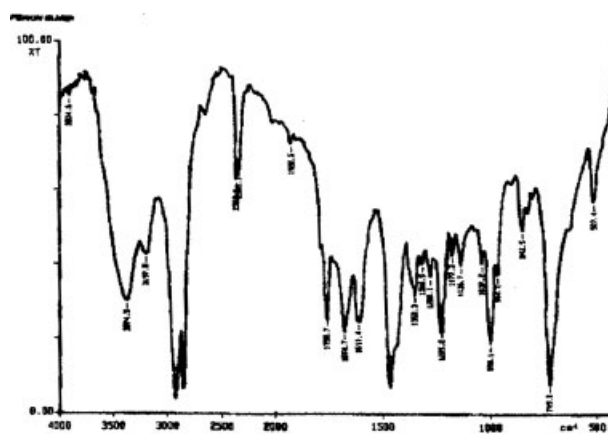


Figure 7 FTIR of PE-g-poly(AAm).

the peaks at 3374.5 and 3197.8 cm^{-1} due to $>\text{N}-\text{H}$ stretching, at 1674.7 cm^{-1} due to amide I, and at 1611.4 cm^{-1} due to amide II in PE-g-poly(AAm) and the peak at 1725.2 cm^{-1} due to $>\text{C}=\text{O}$ stretching in PE-g-poly(AAc) are absent for the unmodified PE. This confirms the formation of the graft copolymers.

TGA

TGA of PE, PE-g-poly(AAm), and PE-g-poly(AAc) was carried out in air at a heating rate of 20°C/min, and the primary thermograms are presented in Figure 9. The initial decomposition temperature (IDT), final decomposition temperature (FDT), and decomposition temperature (DT) at every 10% weight loss are presented in Table I.

The respective thermograms indicate that all three samples showed single-stage decomposition. The grafted samples showed a kink between 120 and 180°C, at which a loss of adsorbed moisture was indicated. The IDTs of the grafted samples, that is, PE-g-poly(AAm) (450°C) and PE-g-poly(AAc)

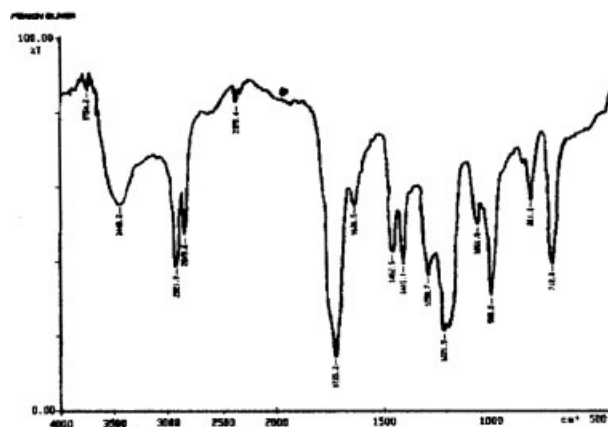


Figure 8 FTIR of PE-g-poly(AAc).

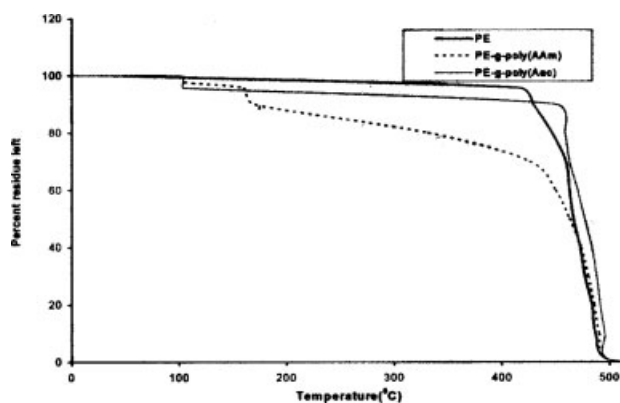


Figure 9 Primary thermograms of PE, PE-g-poly(AAm), and PE-g-poly(AAc).

(434.78°C), were higher than that of unmodified PE (423.9°C). The IDT of the grafts began after weight losses of 10 and 25%, respectively, because of moisture desorption. The FDTs of the grafted samples [504.35 and 500°C for PE-g-poly(AAm) and PE-g-poly(AAc), respectively] were also higher than that of PE (493.83°C). The DT values at every 10% weight loss of PE-g-poly(AAm) were higher than those of PE and PE-g-poly(AAc). The latter, however, had higher DT values beyond a 50% weight loss. It was further observed that the difference in the temperature for every 10% weight loss in the case of PE was a little higher up to a 30% weight loss in comparison with PE-g-poly(AAm). Beyond 30%, this difference fell almost in the same range. However, in the case of PE-g-poly(AAc), although the DT values were lower than those of PE and PE-g-poly(AAm), the temperature difference between each 10% weight loss was much higher up to a 70% weight loss and became the same as that of PE or PE-g-poly(AAm). The lower DT values of PE-g-poly(AAc) were attributed to the fact that the neighboring pendant —COOH groups easily lost water upon heating and produced anhydrides, which were quite stable. This may be the reason for the larger temperature difference between the DT values of each 10% weight loss of PE-g-poly(AAc). The pendant amide functions of grafted PE-g-poly(AAm) also lost ammonia; this pro-

duced imide groupings that, being stable, gave higher DT values.

The higher IDT and FDT values of the grafted samples indicate that grafting improves the thermal behavior of PE. The higher DT values of PE-g-poly(AAm) and the higher temperature difference between every DT value of PE-g-poly(AAc) also support the better thermal stability of the grafted samples.

Biodegradation studies

Biodegradation is an event that occurs through the action of enzymes and/or chemical decomposition associated with living organisms (bacteria, fungi, etc.) or their secretion products. *Biodegradation* might be better used as a term only when it is essential to distinguish clearly between the action of living organisms and other degradation modes (e.g., photolysis, oxidation, and hydrolysis). The main attacking agents in biodegradation are microorganisms, that is, actinomycetes, fungi, bacteria, and so forth, which are widespread in soil, water, and air. One of the potential approaches to rendering synthetic polymers susceptible to microorganisms is to incorporate biodegradable structural units^{9,10} into the polymer backbone.

To find out that whether the grafting of AAm and AAc onto PE with a PTC would render PE biodegradable or not, the biodegradation of grafted samples, that is, PE-g-poly(AAm) and PE-g-poly(AAc), was studied through weight loss in a soil-burial test, and the results were compared with those for unmodified PE.

A few samples of PE-g-poly(AAm) were also prepared with different methods of graft copolymerization, such as chemical-induced, UV-induced, and γ -radiation-induced graft copolymerizations, and they were also tested for biodegradability.

Different samples of the two monomers (AAm and AAc) of various P_g values prepared by the PTC method and an unmodified PE sample were placed into separate tubes containing weighed garden-soil samples. The tubes were tightly closed and kept in the open. The tubes were weighed after regular time

TABLE I
TGA of PE, PE-g-Poly(AAm), and PE-g-Poly(AAc)

Sample	IDT (°C) ^a	FDT (°C) ^a	DT (°C) at every 10% weight loss								
			10%	20%	30%	40%	50%	60%	70%	80%	90%
PE	423.91 (4.29%)	497.83 (99.29%)	429.35	446.74	459.78	463.04	466.74	472.83	477.17	483.69	486.9
PE-g-poly(AAm)	450 (10%)	504.35 (-1.67%)	450.00	458.69	463.04	470.65	477.17	483.69	488.04	491.30	495.65
PE-g-poly(AAc)	434.78 (25.9%)	500 (99.64%)	170.65	331.52	426.09	450.00	463.04	473.91	480.43	485.87	490.22

^a The weight losses are shown in parentheses.

intervals. A reference tube containing only the garden soil was also taken. Any weight loss in the tube containing garden soil was taken into account, and the weight loss of the sample tubes containing the grafted samples was noted.

The weight loss (%) in all the tubes was plotted against the number of days (Fig. 10). Figure 10 shows that all the samples of PE grafted with AAm and AAc showed a rapid decrease in the weight in the first 20 days; the weight became constant up to 35–37 days, after which a further loss in the weight was observed. The maximum weight loss for PE-g-poly(AAm) was observed with $P_g = 50\%$, whereas the PE-g-poly(AAc) sample with $P_g = 10\%$ showed the maximum weight loss. The weight loss decreased with an increase in the number of days, and this indicated that after the initial weight loss, the samples became almost stable and were not affected by the environmental conditions. The weight loss (%) in the first 8 days may have been due to the minor attack of the microorganisms, which helped in the loss of some small molecules. The degradation process did not continue for the rest of the molecules. This may have been due to the lack of proper conditions, such as the optimum water balance, pH, temperature, and open area, required for degradation.

A plot of the weight loss (%) as a function of P_g (Fig. 11) shows that the sample with a lower P_g value had a higher weight loss. Samples of PE grafted with AAc showed higher weight losses than samples of PE grafted with AAm. This occurred because the amide function was more stable toward hydrolysis than the $-\text{COOH}$ group.

Different samples of PE-g-poly(AAm) prepared by photochemical-induced, chemical-induced, and γ -radiation-induced graft copolymerization methods were also subjected to soil-burial tests. The weight loss was noted after regular intervals. The samples prepared by the chemical method, with ceric ammo-

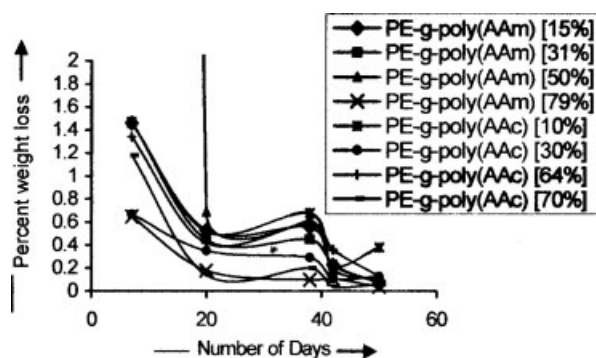


Figure 10 Biodegradation study.

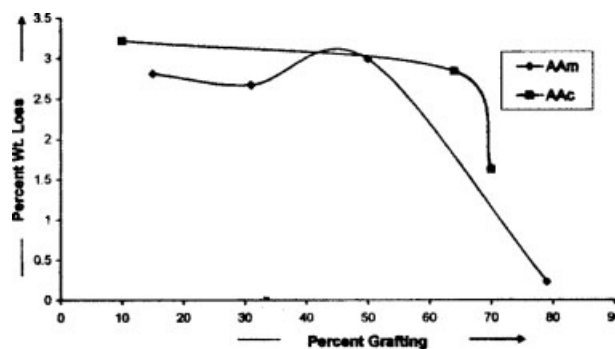


Figure 11 Biodegradation studies of PE-g-poly(AAm) and PE-g-poly(AAc) samples.

nium nitrate (CAN)/ HNO_3 as a redox initiator, and by the γ -radiation method showed initial weight losses of 0.92 and 1.03%, respectively, in the first 13 days; the γ -radiation sample remained constant for the next 43 days, whereas a small weight loss of 0.32% was observed for the CAN sample. No change in the weight was observed for the sample prepared by the photochemical method.

These observations indicate that the synthesis method of the graft copolymer also plays an important role. Grafted samples prepared by the PTC method showed better results than samples prepared by the chemical method, γ -radiation method, or photochemical method. The reason for the easier and greater degradation of the PE graft copolymer prepared by the PTC method is that in this method, the monomer is shifted from the aqueous phase to the organic phase as a single unit; therefore, its attachment to the active site on the polymeric backbone is homogeneous and not haphazard as in other methods, in which the monomer and polymeric backbone are present in the same solvent system. In such systems, the attachment of the monomer or growing polymeric chain takes place anywhere on the backbone polymer, giving a highly branched product. The degradation of a branched system takes place at a much lower rate than that of a long-chain polymer.

For the qualitative determination of the role of the pH, a drop of very dilute acetic acid was added to two sample tubes containing PE-g-poly(AAm) and two sample tubes containing PE-g-poly(AAc). Similarly, a very dilute solution of sodium hydroxide was added to two sample tubes containing PE-g-poly(AAm) and two sample tubes containing PE-g-poly(AAc). The weight loss (%) was noted. The weight loss in the tubes containing PE grafted with AAm to which acetic acid was added was higher than the weight loss in the tubes containing sodium hydroxide. On the other hand, a negligible weight loss was observed for the samples of PE-g-

poly(AAc) containing either acetic acid or sodium hydroxide.

However, a detailed study is needed to actually determine the weight loss as a function of pH.

CONCLUSIONS

Phase-transfer-catalyzed graft copolymerization has been successfully achieved using water-insoluble polymer initiator and water-soluble monomers. The degradation of PE grafted with poly(AAm) and poly(AAc) was also witnessed. Although no definite conclusions can be drawn from this degradation study, it is reasonable to expect that the presence of relatively low-molecular-weight molecules or increased hydrophilicity of the copolymers by grafting might improve the susceptibility of the polymers to microorganisms.

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