pH-Sensitive Biodegradability of Poly(Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-Adipic acid) for Smart Release of Fertilizers

Abu Mahmud[1,*], Anjuman Ara Khatun[2], M. Abdul Matin[1], Monishita Nuzhat Chowdhury and M. Asadul Hoque[1]

[1]*Department of Materials Science and Engineering, University of Rajshahi, Rajshahi-6205, Bangladesh*

[2]*Researcher (Postdoctoral fellow), Center for Crystal Science and Technology, University of Yamanashi, Japan*

Abstract: Poly(Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-Adipic acid) was synthesized in xylene medium using Dean-Stark apparatus. Corresponding monomers were taken in stoichiometric ratios. A trace amount of anhydrous ferric chloride was added as catalyst. The reaction temperature and time were 135-140°C and 5 hours respectively. The synthesized co-polyester was characterized by its solubility test in common organic solvents, molecular weight, FTIR-spectrum, TGA, hydrolytic test and soil burial biodegradability tests. The end group analysis and viscosity methods were used for molecular weight determination. From the hydrolytic degradation study it was found that the polyester sample remained almost intact in the acid medium but gradually degraded in the basic medium. Soil burial test reveals that the co-polyester is almost mixed with the soil within two months which indicates its biodegradability in the soil. Because of these special characteristics this co-polyester could be a future endeavor for smart release of fertilizers.

Keyword: Poly(Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-adipic acid), Hydrolytic test, pH responsive behavior, Soil burial test, Biodegradability, Smart release of fertilizers.

INTRODUCTION

Green polymers or eco-friendly polymers or biodegradable polymers are becoming one of the leading edges of research in polymer science. After being used, biodegradable polymers break down by enzymatic action of microorganisms or by other natural stimulus, leaving non-toxic or eco-friendly byproducts. Researchers focus on stimuli-responsive polymers exhibiting sensitive swelling transitions dependent on various stimuli, *e.g*. pH [1-3], temperature [4], electric field [5], or other chemicals [6]. These polymers have various beneficial applications in biomedicine (colon targeted and gastro-resistance and/or retentive drug delivery systems) and in agriculture (controlled release of insecticide, pesticide and fertilizer) [7-8].

For medical, agriculture and ecological uses it is desirable to have a biodegradable polymer that will undergo degradation in the physiological environment or by the microbial action in the soil. The polymer industry has scope for developments during the coming years because of a pivotal role it can play on bio-medical engineering for medicine and surgery, biodegradable or bio-assailable polymers when used as inserts hold tissue in place while the wounds heal and which then are slowly degrade at the same rate as the new tissue is laid down [9].

*Address correspondence to this author at the Green Materials Laboratory, Department of Materials Science and Engineering, 4th Science Building, University of Rajshahi, Rajshahi-6205, Bangladesh; Tel: +8801912609677; E-mail: mahmud.matsc@ru.ac.bd

It is however, expected that presently available polymer systems with varied and special characteristics should allow increasingly successful applications to solve many problem in the field of the biomedical and agriculture [10-13].

Proper use of fertilizers is very important for predominantly agriculture based country like Bangladesh. But due to a heavy rainfall and improper irrigation, leaching losses of the applied fertilizers and insecticides is very common and sometimes it reaches up to 50%. Successful crop production together with sound soil health can be achieved by balanced fertilization. The Gangetic alluvial soils occupy around 80% of the territory of Bangladesh which have pH greater than 7.5, reaching at times up to 8.3. These soils contain free carbonates and bicarbonates. Thus agriculture is offering a new fertile field for the development of new biodegradable polymers having pH dependent degradation behavior as a carrier that can help to hinder the losses as well as pollution of lake streams occurred by the run-off fertilizers, insecticides, pesticides and fungicides. The successful application of pH dependent biodegradable polymers for the slow release of these substances might be effective for purity of our natural water and decrease agricultural cost [14-19].

Maleic acid is used for various drug intermediates and the biomedical applications of other monomers of the corresponding co-polyester are also known [20]. Taking these pharmaceutically safe monomers we

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have tried to synthesize poly(Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-Adipic acid) and to characterize by solubility test, molecular weight determination, IR-spectra, thermogravimetric analysis, hydrolytic test and soil burial test.

EXPERIMENTAL

Materials

All of the chemicals were analytical grade reagent are employed in the present investigation from BDH-Chemicals Ltd. or E. Merck, Germany. The catalyst (Anhydrous $FeCl_3$) was freshly sublimed before use.

Synthesis of the Polymer

Poly(Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-adipic acid) (PMMBA) was synthesized taking the stoichiometric proportions of its corresponding monomers. Anhydrous $FeCl_3$ (approximately o.4% of the total weight of the monomers) and 80-90 ml xylene were also taken in a 250ml round bottom flask as a catalyst and reaction medium respectively. One or two fragments of pumice stone were added to the flask and the flask was placed in an electrical heating mantle. The central neck of the flask was attached to a Dean-Stark apparatus. Then the reaction flask was heated at 135^0C-140°C gently for 5 hours. As the polyester formed by the poly condensation reaction, water (the reaction byproduct) eliminated along with xylene (reaction medium) as an azeotropic mixture. The synthesized polymer was collected from the round bottom flask by dissolving it in acetone and purified by precipitating using water as non-solvent. The purified co-polyester was vacuum dried at 60°C and stored in desiccators [21].

Characterization

PMMBA was characterized by its solubility in common organic solvents at the ambient temperature, FTIR spectrum, TGA, molecular weights, hydrolytic degradation test and soil burial test. The polyester was insoluble in water but readily soluble in acetone, ethyl acetate and mixed solvent (toluene: ethanol, 1:3). FTIR spectrum of the polymer was recorded using an IR Spectrophotometer (Model: IR Prestige 21, 500-4000 cm^{-1}).

Molecular Weight Determination

The precipitation technique was used for fractionation of the synthesized co-polyester at (20±1) $^\circ$C. Here acetone was used as a solvent and water as a non-solvent. End group analysis $\left(\bar{M}_n\right)$ and viscosity measurement $\left(\bar{M}_V\right)$ were used for determination the molecular weights of these fractions. For end group analysis, a precisely weighed quantity (less than 0.8 g) of the polyester sample was dissolve in 1:3 mixed solvent of toluene and ethanol. This was titrated against 0.1 (N) alcoholic potassium hydroxide solution using phenolphthalein as indicator. The end point was the appearance of a slightly pink color [22]. On the other hand, for viscosity average molecular weights, a number of very dilute solutions of different known concentrations (g/ml) of each fraction of the polymer sample were made in acetone. The solvent and the solution flow time for different concentrations were measured using Oswald's viscometer. For each concentration, the corresponding reduced viscosity was calculated and graphed (reduced viscosity vs. concentration) which was extrapolated to zero concentration. The common ordinate intercept of these graphs gave the intrinsic viscosity. Finally the logarithms of the intrinsic viscosities of these polymer fractions were plotted against the logarithms of their molecular weights $\left(\bar{M}_n\right)$ and a linear curve was obtained. The ordinate intercept and the slope of the curve gave the values of constants 'K' and 'α' respectively. The molecular weight $\left(\bar{M}_V\right)$ of the polymer samples were calculated by putting the values of 'K' and 'α' in the Mark-Houwink equation, $\left[\eta\right] = K\left(\bar{M}_v\right)^a$ [23].

Hydrolytic Degradation Study

The pH responsive characteristic of the synthesized co-polyester was observed by hydrolytic degradation test in different pH values. Polyester samples were cut into suitable slices and were placed in solutions of different pH values in separate conical flasks. Conical flasks were sealed with rubber corks. After one hour intervals, its pH was measured up to 5 hours by a pH-meter at room temperature (30°C). Results were plotter in graph and compared with blank solutions. Hydrochloric acid and sodium carbonate were used to prepare solutions of different pH values. The change of pH of the polymer sample containing solutions with respect to time was considered as an indication of the degradation of the polyester.

Soil Burial Biodegradability Test

Soil burial test was carried out according to the procedure used by Rumi *et al* [24] with minor modification. For this purpose a number of beakers

(250ml) were taken and filled with color soil from the garden. The soil in the beakers were blended properly and a polymer sample weighing about 0.2g was placed in the mid of each of the beakers. The soils in the beakers were kept constantly wet with water. The beakers were numbered for each of the samples to provide identity. Then alter regular intervals of 7 days one of the beakers was taken out and the polymer placed on it was found out, washed gently with water to remove soil adhered on its surface and then dried at 60°C under vacuum until constant weight was obtained. Weight loss of the polymer in the soil with respect to time was recorded as a mark of its degradation. Three sets were taken together and their average results were taken into account. The pH of the soil was monitored regularly throughout the experiment.

Thermo-Gravimetric Analysis

Thermo-gravimetric analysis was carried out to evaluate the thermal stability of the polymer [25]. This was done using an EXSTAR 6000, TG/DTA 6300 thermal analyzer instrument. Measurements were performed under nitrogen atmosphere, in the temperature range from 25 to 600°C, at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

Synthesis

To synthesize the co-polyester, the mole ratio of the monomers was kept as maleic acid: malic acid: adipic acid: butane-1,4-diol =1: 1.25 :1 :3. Malic acid was taken 20% higher than the expected stoichiometric ratio because individual studies show that around 20% of malic acid undergoes self polycondensation with its own secondary hydroxyl groups [21]. Theoretically 50% of the carboxyl groups should take part in such reaction in but it happens so probably because of steric effect. The reaction equation of the synthesized co-polyester and the expected structure of PMMBA would be as shown below in Figure **1**:

The synthesized PMMBA was solid, pale orange in color and sticky at room temperature.

FTIR Characterization

The broad band representing the -OH group at the region 3100-3400 cm^{-1} in the spectrum of the diol is almost absent in the spectrum of the polymer (Figure **2**). The >C=0 stretching frequency at the region 1700-1720 cm^{-1} of the spectra of di-acids shifted to 1724.36 cm^{-1} and a new band representing the ester linkage appeared at 1166.93 cm^{-1} in the spectrum of the polymer (Figure **2**). All these indicate the reaction between -OH and -COOH groups forming ester linkages [26-27].

Molecular Weight

Values of intrinsic viscosities of various polymer fractions are provided in Table **1**. The MHS (Mark-Hauwink-Sakurada) constants of PMMBA are 'K' = 4.17×10^{-3} ml/g and 'α' = 0.74 respectively. According to Mark-Hauwink equation, the relationship between viscosity average molecular weight and intrinsic viscosity [28] can be expressed as, $[\eta] = 4.17\times10^{-3}[\bar{M}]^{0.74}$ [29-30].

Thermo-Gravimetric Analysis (TGA)

Figure **3** shows the TG/DTA curve of PMMBA. The decomposition process consists of three regions. Owing to the initial breakdown of the complex and spontaneous combustion, the first weight loss region is observed at 25–250 ºC for the co-polyester which indicates the evaporation of absorbed water. With the liberation of H_2O and CO_2 providing an oxidizing environment for the combustion of the organic components. The spontaneous combustion is caused from different ions in the sample. The second weight loss region observed at 250-500 ºC. It was ascribed to

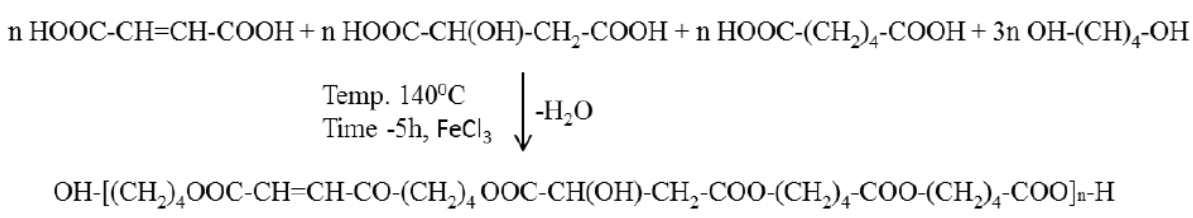

Figure 1: Synthesis of Poly(Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-Adipic acid).

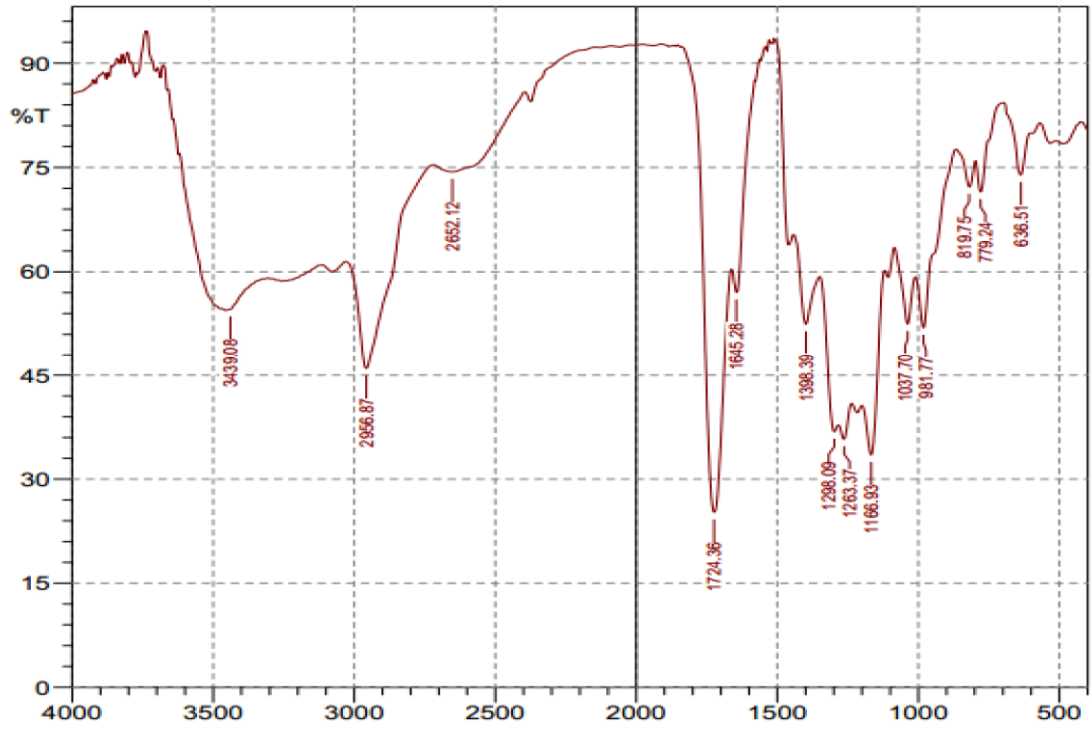

Figure 2: FTIR Spectra of Poly (Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-Adipic acid).

Table 1: Characterization of Poly(Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-adipic acid) by Viscosity Average Molecular Weight $\left(\bar{M}_v\right)$

Polymer Fraction no.	Values of k and α (acetone at 30°C)[a]		Intrinsic Viscosity [η] ml/g	Molecular Weight from Mark-Houwink Relationship
	K x 10^3 ml/g	α		
I	4.17	0.74	7.10	23475
II			6.40	19820
III			5.40	15941
IV			4.80	13644
V			4.0	11320

[a] k and α are the MHS (Mark-Hauwink-Sakurada) constants.

dehydration of -OH group in the polyester structure that lead to two degradation systems involving both inter and intra-molecular transfer reaction, the oxidation of complexes. The third weight loss region in the temperature range 500– 600 ºC which is believed to be due to the formation of corresponding phase. Above 600 ºC there is no weight loss. From this study, it is seen that the TGA curve is steady, demonstrating the absolute volatility of water, organic compound and the completion of crystallization route. From Figure **3** it is shown that the glass transition temperature of PMMBA is 61.1 ºC.

Hydrolytic Test

At room temperature, hydrolytic degradation study (Figure **4**) in solutions of different pH values showed that this co-polyester remained almost intact in solutions of pH 0-3.0, slight degradation was observed in pH range 3.0-6.0 but they gradually degraded in solutions of pH>6.0. In acid region the polymer samples swell insignificantly. But in alkaline region they swell and the ester linkage is hydrolyzed resulting the meaningful decrease in the pH of the polymer sample containing solutions with respect to time.

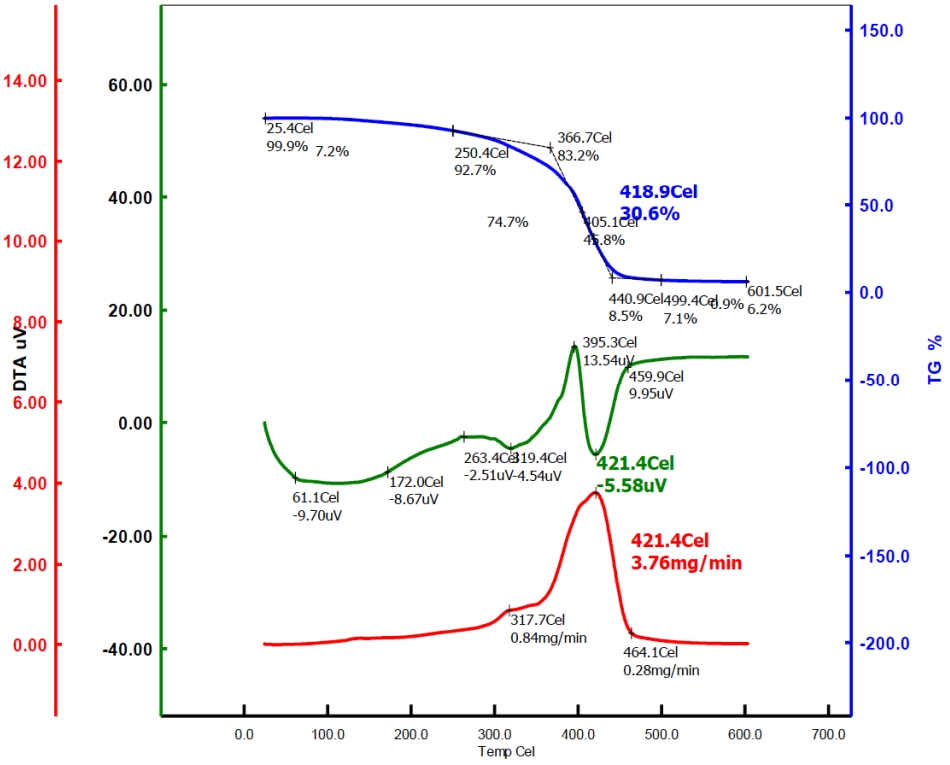

Figure 3: TGA/DTA curve of Poly(maleic acid-co-malic acid-co-butane-1,4-diol-co-adipic acid).

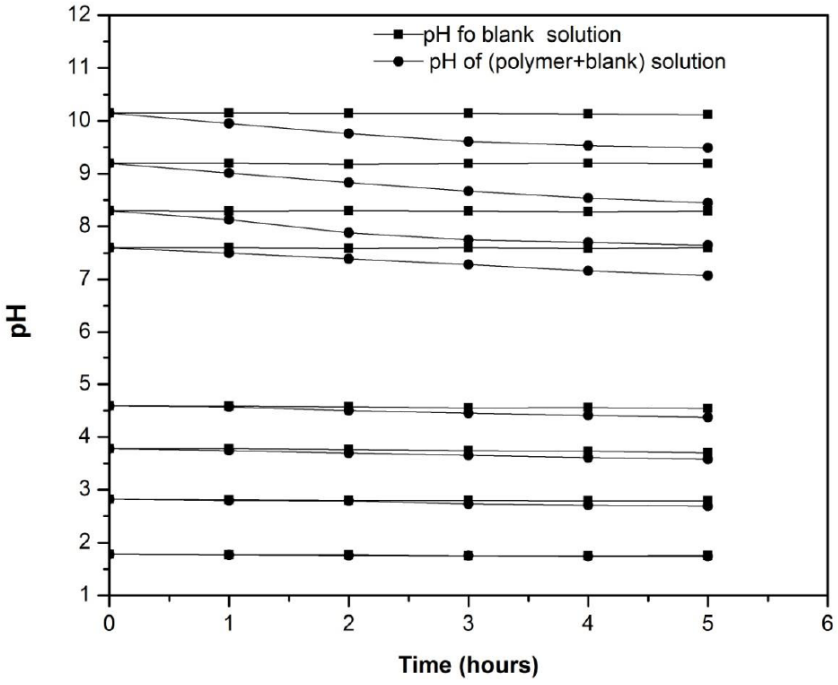

Figure 4: pH Vs time plots for Poly (Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-Adipic acid) in hydrochloric acid and sodium carbonate solution of different pH at 25^0C.

Soil Degradation Test

Figure **5** shows that polymer buried in soil loses weights gradually and after 56 days it ultimately mixed with the soil indicating its total gradual degradation in the soil. Few factors simultaneously play decisive role for such degradation. The average pH of the soil during the experiment was found around 7.5. pH of the soil

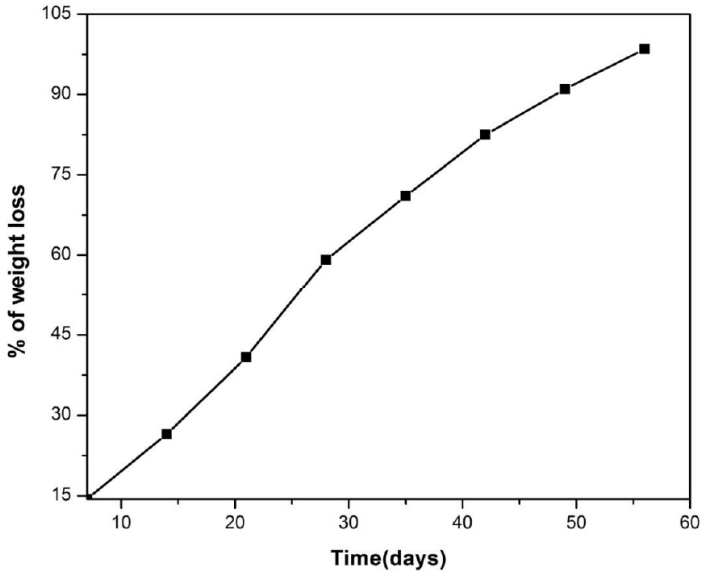

Figure 5: Soil degradation of maleic acid malic acid butane-1,4, diol co-polyester at normal weathering condition.

and enzymic action of the soil borne microorganisms are possibly two predominant factors for this slow and gradual degradation of the co-polyester [31-34].

CONCLUSION

In this article, pH responsive biodegradable nature of Poly(maleic acid-co-malic acid-co-butane-1,4-diol-co-adipic acid) is reported. As this co-polyester slowly degraded in soil, it could be the best candidate for the carrier of controlled release of impregnated insecticides, pesticides and fertilizers. But more tests are yet to be done to measure its performance in the field of agriculture.

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ABBREVIATIONS

PMMBA for Poly(Maleic acid-co-Malic acid-co-Butane-1,4-diol-co-adipic acid).

CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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