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### Comparison Between Physical Blending and Copolymerization of Poly(Trimethylene Carbonate) and Poly(Adipic Anhydride) with Special Regard to Compatibility, Morphology and Degradation

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## COMPARISON BETWEEN PHYSICAL BLENDING AND COPOLYMERIZATION OF POLY(TRIMETHYLENE CARBONATE) AND POLY(ADIPIC ANHYDRIDE) WITH SPECIAL REGARD TO COMPATIBILITY, MORPHOLOGY AND DEGRADATION

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Key Words: Poly(trimethylene carbonate), Poly(adipic anhydride), Degradable blend, *in vitro* Degradation, Hydrolysis

### ABSTRACT

Blends from poly(trimethylene carbonate) (PTMC) and poly(adipic anhydride) (PAA) with different compositions and different molecular weights were prepared by a solution blending method. Comparing blends with copolymers generally, the original degradation properties of the used components were changed through physical blending (or filling an oligomer as a plasticizer into a polymer), which represents a more convenient, lower cost and composition-controlled method to combine two components with different degradation properties. DSC results show that the  $T_g$  of PTMC and  $T_m$  of PAA in the blend are lower than those in the homopolymers and they are functions of the molecular weight for PTMC in the blends. SEM micrographs show that a thick dispersion occurs in the blends. The molecular weight of PTMC in the blend obviously decreases as the degradation *in vitro* proceeds, for the samples of 40% PTMC,  $M_n$

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drops 39%,  $M_w$  drops 12% and the polydispersity increase 44% within 25 days. GC-MS and DSC measurements imply that the depression in molecular weight of PTMC is attributed to the formation of PTMC oligomers from degradation. The results confirmed that the filling of PAA oligomers, which acted as a fast-degraded plasticizer and resulted in an acidic environment, to PTMC could speed up the degradation of PTMC in phosphate buffer solution. Degradation rate and pH of the degradation media change depending on the composition of the blends.

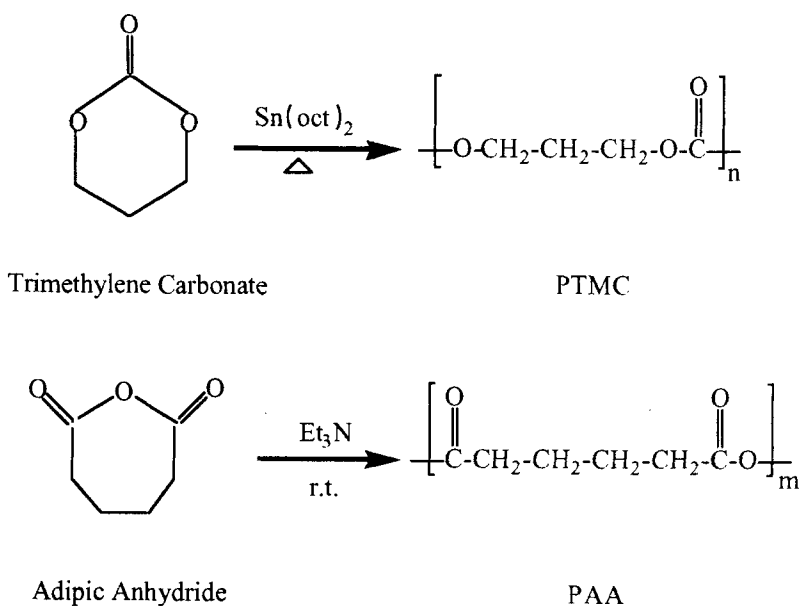
## INTRODUCTION

Physically blending of two or more polymers (or filling some low molecular weight oligomers as the plasticizer into another polymer) in contrast to copolymerization is a more convenient, lower cost and composition-controlled route to achieve materials with different properties than the homopolymers and has also attracted considerable commercial utilization [1-5]. Totally miscible homopolymers are microscopically homogeneous (i.e. mixed on a molecular scale), and partially miscible blends display microscopic heterogeneity. Conversely, immiscible blends are macroscopically heterogeneous and display multiphase behavior.

Although extensive research has been devoted to the formation and characterization of blends of various polymers, not much attention was given to the formation and characterization of partially miscible blends of biodegradable (bioerodible or absorbable) polymers for biomedical applications and environmentally friendly packing materials, especially those containing polyanhydrides [5-8].

The linear aliphatic polycarbonates are known to be biodegradable and biocompatible and used in degradable sutures, such as **Maxon**<sup>®</sup>, a trimethylene carbonate-glycolide block copolymer [9]. PTMC has a good elasticity at room temperature [10]. However, it degrades unexpectedly slow (several years) unaffected by initial molecular weight, ionic strength of the water, storage temperature and shaking motions. Their degradation mechanisms have been attributed to a simple hydrolytic process [11].

The polymers made of linear diacid fats were also biocompatible and degradable [4]. The degradation product of the polymer, adipic acid, was not expected to have any adverse effects in the precorneal area, which is important for an *in vivo* application [12]. After absorption by the system, the adipic acid is expected to be metabolized by  $\beta$ -oxidation of fatty acids. The *in vitro* study of poly(adipic anhydride), however, revealed a surprisingly fast degradation (one day) [11,13].



Scheme 1

To combine two materials with quite different degradation properties poly(trimethylene carbonate) (PTMC) and poly(adipic anhydride) (PAA) system was studied. The following homopolymers were synthesized: a) poly(trimethylene carbonate) with different molecular weight, b) poly(adipic anhydride) and the monomer of adipic anhydride from acetic anhydride and adipic acid. All polymers were synthesized using ring-opening polymerization of the corresponding cyclic monomer structure, according to Scheme 1.

PTMC homopolymers with different molecular weight were synthesized using the same initiator at the same monomer/initiator molar ratio, the same reaction time and different temperatures (Table 1). PAA oligomers have quite low molecular weights caused by the formation of an addition product involving the etheric oxygen of one anhydride bond and the carbonyl carbon of another [14].

A series of blends of poly(trimethylene carbonate) and poly(adipic anhydride) with different composition ratio between 0 and 100% PTMC was prepared by a solution blending method. Blends of PTMC with different molecular weight and PAA were prepared in the same procedure as well.

The objective of this paper is to compare physical blending or plasticization by oligomers to copolymerization with special regard to the compatibility, the

TABLE 1

Sample Series No.	Polymer	$M_n$ (g/mol)	$M_w$ (g/mol)	$M_w/M_n$
1	PTMC	63 838	149 745	2.35
2	PTMC	80 785	136 317	1.69
3	PTMC	39 318	67 359	1.71
4	PTMC	41 517	65 988	1.59
5	PTMC <sup>a</sup>	7 608 <sup>a</sup>	16 248 <sup>a</sup>	2.14 <sup>a</sup>
6	PTMC <sup>a</sup>	41 601 <sup>a</sup>	76 984 <sup>a</sup>	1.85 <sup>a</sup>
7	PTMC	47 767	77 513	1.62
8	PTMC	27 855	38 790	1.39
9	PAA	516	936	1.81
10	PAA	646	971	1.51
11	PAA	516	791	1.53

<sup>a</sup> Solution polymerization,  $AlCl_3$  as initiator in toluene, 80°C, Ar atmosphere.

morphology and the *in vitro* degradation properties of a PTMC/PAA system, and to study whether, and in which direction, a fast-degradable component (PA oligomer) would affect a slow-degradable one (PTMC) when they were mixed.

## EXPERIMENTAL

### Materials

1,3-Propandiol p.a. (Merck-Schuchardt, Germany), diethyl carbonate p.a. (Aldrich Chemical Co., USA), stannous octoate (stannous 2-ethylhexanoate,  $Sn(oct)_2$ ) (Aldrich Chemical Co., or Sigma Comp., USA), adipic acid p.a. (Merck-Schuchardt, Germany), acetic anhydride p.a. (Riedel-de Haen AG, Germany), triethylamine  $Et_3N$  (Merck-Schuchardt, Germany), toluene (p.a.), dichloromethane  $CH_2Cl_2$  (p.a.), methanol (p.a.) and petroleum ether (b.p. 30-50°C) and *n*-hexane (p.a.) were used as received unless otherwise mentioned.

### Instrumental Methods

Waters size exclusion chromatography SEC equipment was used to determine the molecular weight and molecular weight distribution. A Waters 6000A pump with five Ultrastyrigel<sup>®</sup> columns ( $10^5$ ,  $10^4$ ,  $10^3$ , 500 and 100 Å in pore sizes) and chloroform as eluent, with a flow rate of 1.0 mL/min, was used at 25°C with a Waters RI 401 refractive index detector. The SEC system was calibrated with polystyrene standards with narrow molecular weight distributions ( $PD = M_w/M_n < 1.09$ ).

Morphological changes were recorded using a Perkin-Elmer Differential Scanning Calorimeter DSC-7. Indium was used as standard for temperature calibration and the analyses were made under a constant stream of nitrogen. The heating rate was 10°C/min and the cooling rate was 40°C/min. Melting and glass transition temperatures as well as the heat of fusion  $\Delta H$  were recorded at the second heating scan to give all the samples the same thermal history.

Morphological or topological changes were also studied on a JEOL JSM-5400 scanning electron microscope. Samples for SEM were mounted on metal stubs and sputter-coated with gold-palladium under argon gas (Denton Vacuum Desc II). The samples were coated for 60 seconds (two pulses of 30 seconds each).

Gas chromatography-mass spectrometry (GC-MS) apparatus used for identification and quantification of degradation products was a Perkin-Elmer 8500 Model with a split/splitless injector, connected to a Perkin-Elmer ion-trap detector (ITD) mass spectrometer. The gas chromatograph was equipped with a DB-1 (dimethyl polysiloxane) and DB-FFAP (nitroterephthalic acid modified polyethylene glycol) capillary columns from J & W (30m x 32mm i.d.). The column was programmed from 60°C to 250°C at 10°C/min. Helium was used as carrier gas. The degradation products were extracted from the incubation buffer solution with C18 solid phase extraction (SPE) columns. The columns were first activated with 1 mL methanol and conditioned with 1 mL phosphate buffer solution (pH=2). Then, the pH of the incubation buffer with unknown water soluble degradation products was adjusted to pH=2 with HCl. 1 mL of the incubation buffer (pH=2) with unknown samples with internal standard compounds (1,4-butanediol for TMC and pimelic acid for adipic acid) was allowed to penetrate through the SPE column. The column was dried slightly and the degradation products were eluted with 1 mL 0.1% HCl in methanol. The 0.1% HCl in methanol fraction was warmed 15 minutes at 60°C to methylize dicarboxylic acids. The methanol fractions were subjected to GC-MS analysis [15].

The pH values of the incubation solution from the degradation series were measured with a Metrohm 632 pH-Meter (Switzerland) with a Metrohm combined glass electrode at 25°C.

### Synthesis of Monomers and Polymers

Monomer: 1,3-Dioxan-2-one TMC was prepared according to the literature [10]. The crude monomer was reprecipitated from toluene to cold *n*-hexane. Yield: 53%. <sup>1</sup>H-NMR: (CDCl<sub>3</sub>), δ=2.15 ppm (quintet, -CH<sub>2</sub>-, 2H), δ=4.44 ppm (t, -OCH<sub>2</sub>-, 4H). TMC is white crystalline compound with a m.p. of 50°C.

Oxepan-2,7-dione AA was prepared according to the literature [11]. <sup>1</sup>H-NMR: (CDCl<sub>3</sub>), δ=2.0 ppm (m, -CH<sub>2</sub>-, 4H), δ=2.75 ppm (m, -(CO)CH<sub>2</sub>-, 4H). AA is a colorless liquid which turns pink upon standing in air at room temperature.

All polymerizations were carried out in 25 mL septum vials with Teflon-coated magnetic stirring bars sealed with a rubber septum dried at 110°C. The monomer was added to the dried vial which was sealed and flushed with the inert gas (Ar). Solid initiators were added together with the monomer, and liquid initiators were added via a syringe. The bottles were immersed in a thermostatic oil bath-stirrer and held at constant temperature for the desired reaction time. The polymers were isolated by dissolving them in dichloromethane and subsequently precipitation in cold CO<sub>2</sub>(s)/methanol (PTMC) and *n*-hexane (PAA) or petroleum ether (PAA) and filtration. The polymers were dried to constant weight at room temperature *in vacuo*. PAA was synthesized from AA in bulk at 25°C for one hour by using triethylamine Et<sub>3</sub>N (0.4mol% or [M]/[I]=250) as the initiator. PTMC was synthesized from TMC in bulk by using Sn(oct)<sub>2</sub> ([M]/[I]=250) as the initiator between 80 to 130°C from 5 to 24 hours. Low molecular weight PTMC (M<sub>n</sub>=7600, M<sub>w</sub>=16250, M<sub>w</sub>/M<sub>n</sub>=2.14) was synthesized by solution polymerization using AlCl<sub>3</sub> as initiator in toluene at 80°C for 24 hours under Ar atmosphere.

### Preparation of Blends

Blends of PTMC and PAA were prepared from the same batches of homopolymers in different composition between 0 and 100% PTMC. 2.0 g of the polymers were dissolved in dichloromethane to form a 10 mL solution. 5 mL of one polymer solution was mixed with 5 mL of a second polymer solution in a sealed 25 mL glass vial and stirred for a complete dissolution. The solvent was evaporated at room temperature under constant stirring. The resulting blends were dried *in vacuo* at room temperature to constant weight.

### ***In vitro* Hydrolytic Degradation of Blends**

Degradation samples were prepared and incubated according to the literature [11,15, 28 and 29]. The circular samples with the surface area ca. 50 mm<sup>2</sup> were placed in individual vials with 10 mL 0.06 M phosphate buffer solution (PBS) pH=7.4 (Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> in 0.9% NaCl solution). The vials were sealed with rubber septa and aluminium caps and placed in a thermostatic oven held at 37°C without shaking motions.

### **Analysis and Measurements**

Samples were withdrawn in duplicate or triplicate at each analysis time and isolated by removal of the buffer solution and dried *in vacuo* until constant weight. The samples were characterized by dry weights, molecular weights, glass transition temperatures ( $T_g$ ), melting temperatures ( $T_m$ ), molecular weight distribution changes, morphological changes. The aqueous medium was analyzed with respect to pH changes and identification and quantification of degradation products. The remaining weight was calculated from the following equation:

$$\% \text{ remaining weight} = \text{measured weight} / \text{original weight} \times 100$$

From the GC-MS results, the amount of degraded PAA was calculated as follows:

$$\% \text{ degraded PAA weight} = \frac{\text{adipic acid weight detected in the incubation buffer solution}}{\text{original PAA weight in the blends}} \times 100$$

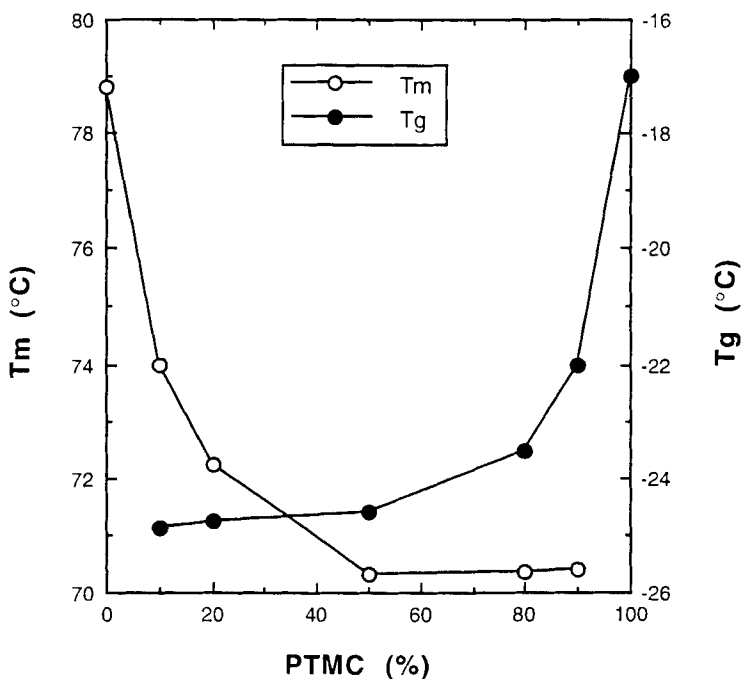
The composition of the degradation samples was determined by SEC, measuring the peak areas corresponding to PTMC and PAA respectively.

## **RESULTS AND DISCUSSION**

DSC results show that the  $T_g$  of PTMC and  $T_m$  of PAA in the blend are lower than those in the homopolymers (Figure 1).

$T_g$  of PTMC was depressed at least 5°C to 8°C.  $T_g$  is -17°C for the PTMC homopolymer and lower than -60°C for the PAA homopolymer. So the  $T_g$  change seems to have a tendency that the glass transition temperatures shifted inward.  $T_m$  was depressed 6°C to 9°C compared to PAA homopolymer ( $T_m=79^\circ\text{C}$ ). The observable depression of the melting temperatures of crystals and glass transition temperatures in miscible blends is widely reported in the literature. Many authors

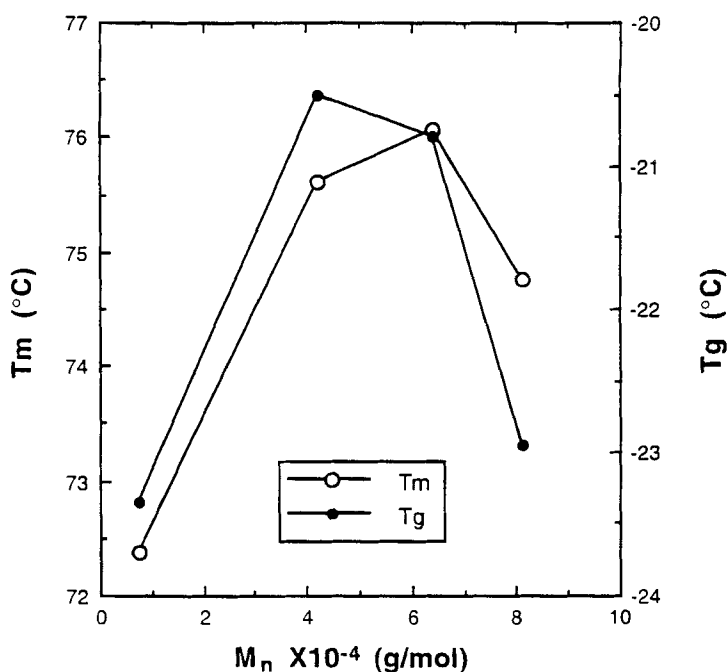




**Figure 1.** Glass transition temperatures ( $T_g$ ) and melting temperatures ( $T_m$ ) measured by DSC for the physical blend from PTMC and PAA as a function of the percentage of PTMC in the polymer blends.

have reported detectable differences between the melting behavior of a semi-crystalline homopolymer and its blends [16-18]. Almost invariably in all cases, the observable melting point of the semi-crystalline homopolymer is depressed in the blends. In our work on the physical blend of PTMC and PCL [3], neither of the glass and melting transitions deviates markedly from the behavior of the homopolymers, due to incompatibility between the two components. However, for the random copolymer series of TMC and  $\epsilon$ -caprolactone,  $T_m$  drops 27°C and  $T_g$  drops 35°C [3]. So the depression of the glass transition temperature of PTMC and the melting temperature of PAA in the blend indicates the plasticization effect of PAA oligomer to PTMC or a partial compatibility between two components. The variable range of  $T_g$  and  $T_m$  increases as follows: incompatible system [blend of PTMC/poly( $\epsilon$ -caprolactone)] < partially compatible system or homopolymer with plasticizers [blend of PTMC/PAA] < copolymer [PTMC-co-poly( $\epsilon$ -caprolactone)].

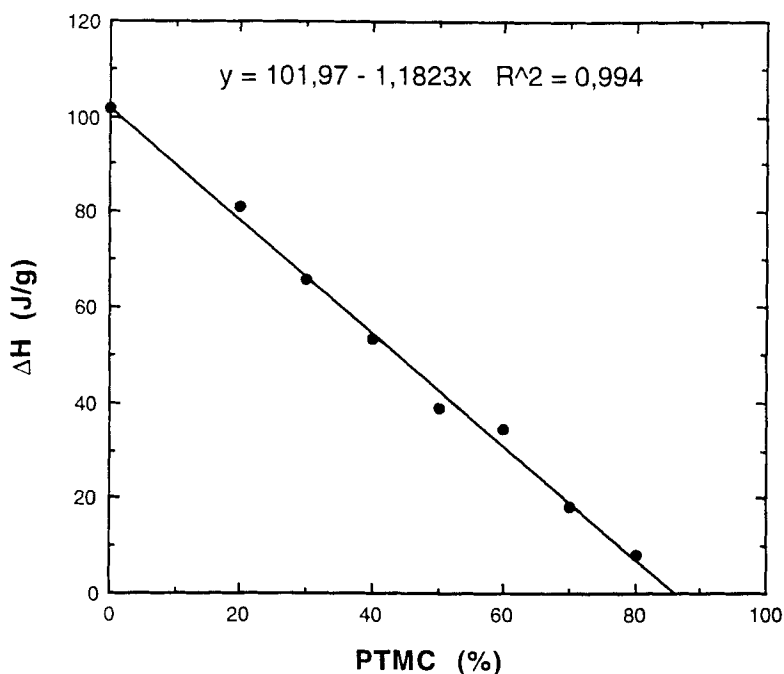
When a small amount of PAA was filled into PTMC, PAA as comparatively smaller particles could be included by PTMC to form comparatively homo-



**Figure 2.** Glass transition temperatures ( $T_g$ ) for PTMC and melting temperatures ( $T_m$ ) for PAA measured by DSC from the PTMC/PAA physical blends as a function of the number average molecular weight of PTMC in the blends.

geneous PTMC phase. The included PAA resulted in  $T_g$  decreasing for PTMC. The amount of PAA that could be included into PTMC is limited because their partial compatibility. When extra amount of PAA was mixed with PTMC, they would gradually form their own continuous PAA phase and hardly give any contribution to the  $T_g$  decreasing for PTMC. The agglomeration of PAA increases with the increasing of PAA so that PAA gradually formed continuous phase.  $T_m$  increases until the  $T_m$  for PAA homopolymer (79°C). And vice versa, e.g.  $T_g$  (over 10 to 80% PTMC range) and  $T_m$  (over the 10 to 80% PAA plasticizer range) values show little change (Figure 1).

This phenomenon is similar to that of poly(ethylene) when it was blended with starch. Smaller particle size and freedom from agglomerates is favorable to achieve an adequately homogeneous morphology. It is probably due to a limited tolerance for both ingredients when a poor compatible plasticizer was added into high molecular weight PTMC with a rubbery character at room temperature [19].

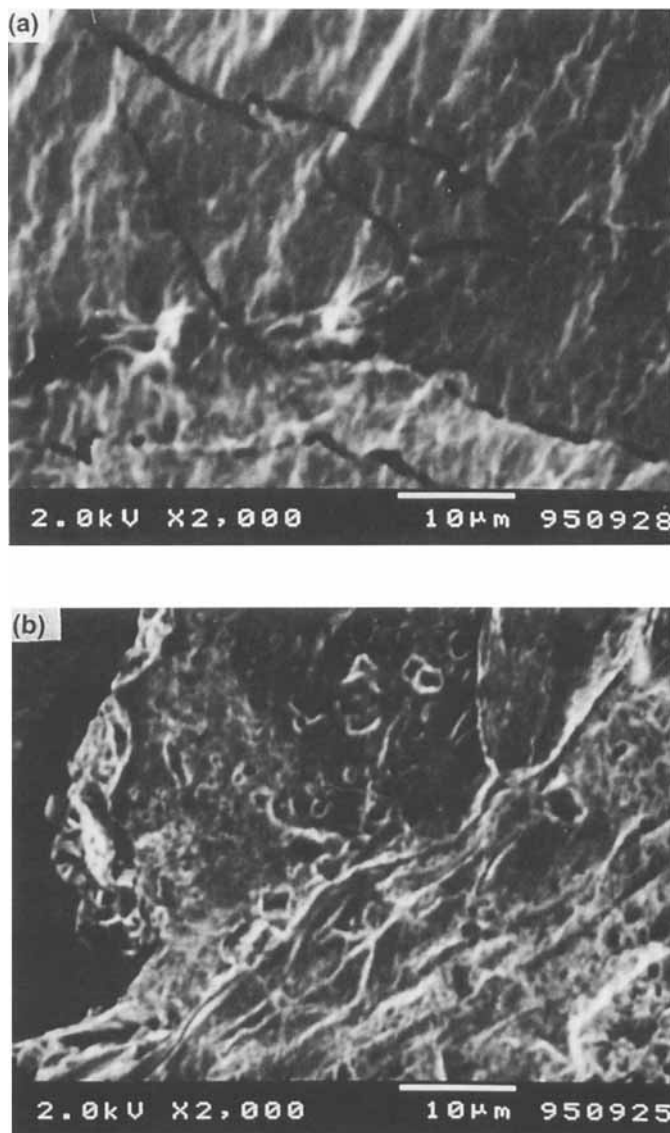


**Figure 3.** Heat of fusion,  $\Delta H$ , for the melting endotherm of PTMC/PAA blends from DSC experiments, as a function of the percentage of PTMC in the blends.

The changes in Figure 1 also implies that there is a phase separation existing in PTMC/PAA blends.

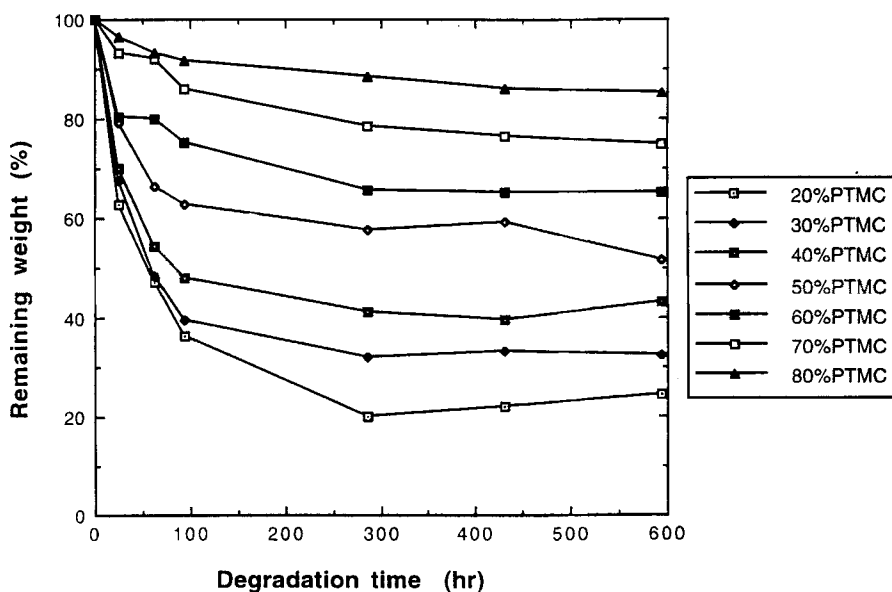
$T_g$  and  $T_m$  of the blends are functions of the molecular weight for PTMC in the blends (Figure 2). The result shows that the compatibility of the two components in the blend or the plasticization effect of PAA oligomer to PTMC is influenced by the molecular weight of PTMC in the blend. In addition, the blends could form uniform and translucent films with elasticity. The results indicate that the blend of PTMC and PAA is uniform macroscopically.

Needless to say, the amount of crystallinity in a semi-crystalline polymer blend is less than that in the corresponding homopolymer. An estimate of the amount of crystallinity in a blend can be made by assuming the area under a crystalline melting curve to be proportional to the level of crystallinity in the polymer [2]. The crystallinity of a blend is directly proportional to the amount of PAA in the blend (Figure 3).



**Figure 4.** SEM micrographs of selected samples: (a) the blend containing 95% PTMC (surface); (b) the blend containing 50% PTMC (surface).

It is reasonable to expect that blend stability depends on morphology. Therefore, the studies of blends morphology might also contribute to better understanding of polymer degradation. In SEM photographs (Figure 4a) a porous topography (with fine holes) surrounded by a more dense, plastic yield zone (mainly

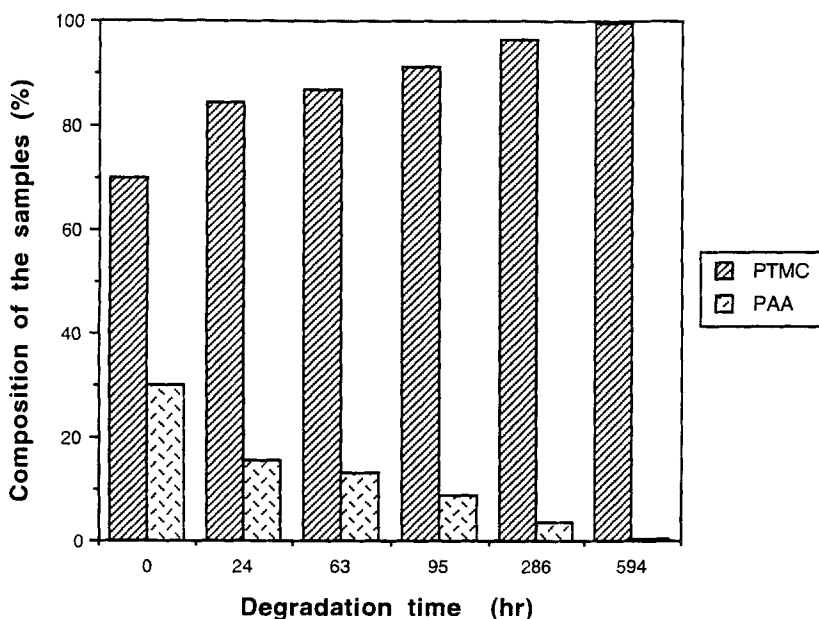


**Figure 5.** Remaining weight in % as a function of the incubation time for PTMC/PAA blend series.

composed of PTMC) can be seen. The porous topographies show the existence of thick dispersion and heterogeneity of the materials, which could reflect phase separation in the samples and incompatibility between PTMC and PAA. The samples with low PAA content has a more homogeneous morphology (Figure 4b). In the event of phase separation, interfacial tension favors a reduction in surface area that leads to macroscopic segregation. One of the driving forces for the separation in polymer mixtures is the difference in surface free energies of the respective components. If polymers reside in separate phases, the interaction is limited to their interface [20]. Interfaces in immiscible blend are often weak, but their adhesion can be improved by the shrinkage of their surfaces. So a morphology from nodules of PAA overlaid by a continuous phase of PTMC is formed.

A degradation test *in vitro* was done. Under the condition of 37°C, in phosphate buffer solution (pH=7.4), the blend samples degrade quickly during a period from one day to 25 days (Figure 5). The degradation is evaluated from the weight loss of the sample, the pH changes of the solution and changes of molecular weight and its distribution of the polymer, and the analysis of degradation products.

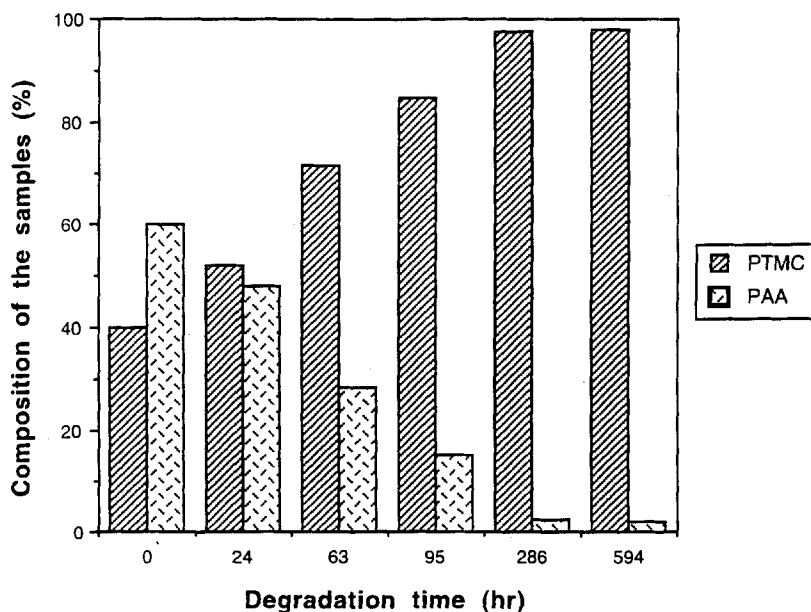
As shown in Figure 5, weight loss increases with incubation time. Weight loss increases faster for the samples with higher PAA content than those with lower



**Figure 6.** Composition of the blends with 70% PTMC from SEC as a function of the incubation time.

PAA content. From Figures 5-7, it could be observed that there is a correlation between sample weight loss and PAA hydrolysis/weight loss. The weight loss of the samples resulted mainly from PAA weight loss due to its degradation or probably its leachability. For example, when the samples with 40% PTMC were incubated for 286 hours, sample weight loss reached about 59%, PAA weight loss is above 98%; The samples with 70% PTMC were incubated for 286 hours, samples weight lost around 21% and PAA lost above 91%. From Figure 5 it could be found that after 300 hours of incubation the sample weight loss keeps almost constant. Based on the analysis for the composition of degradation samples, at that time almost all samples lost their PAA above 90%. Due to the slow degradation of PTMC, the sample weight remains nearly an invariable value after 300 hours of incubation.

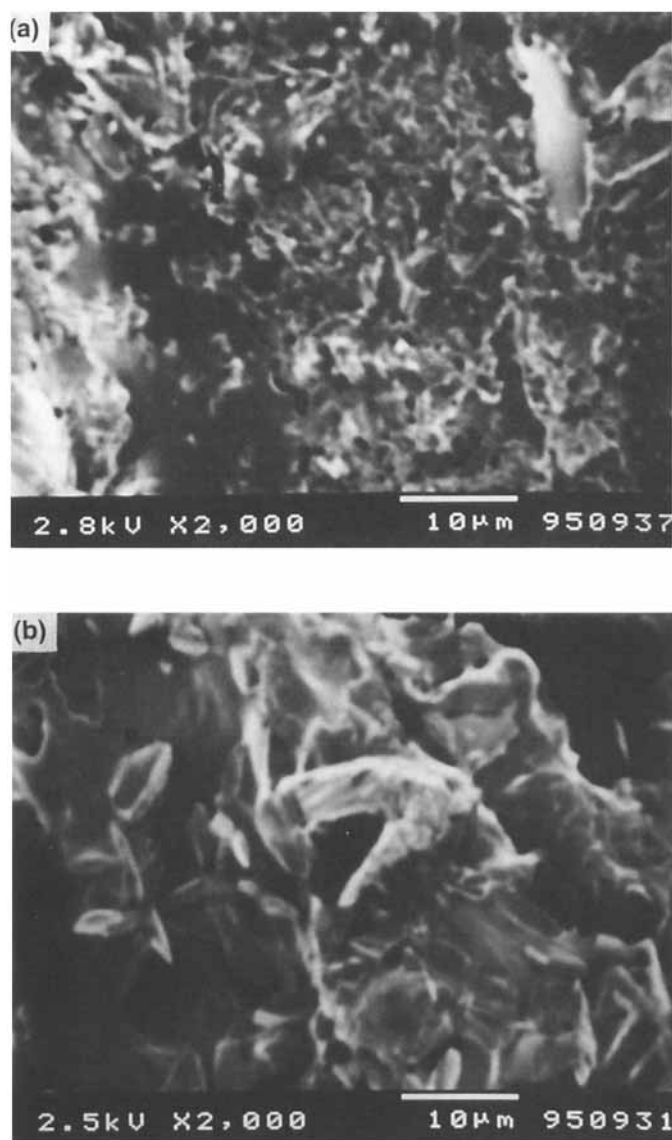
The degradation of PAA in bulk of matrix could create an acidic micro-environment, which makes it possible that PTMC in bulk degraded. From Figures 6 and 7, even in samples with low PAA content, there still is a small amount of undegraded PAA, which implied that a small amount of PAA was included in PTMC phase, after 600 hours of degradation. The included PAA needs a pathway



**Figure 7.** Composition of the blends with 40% PTMC from SEC as a function of the incubation time.

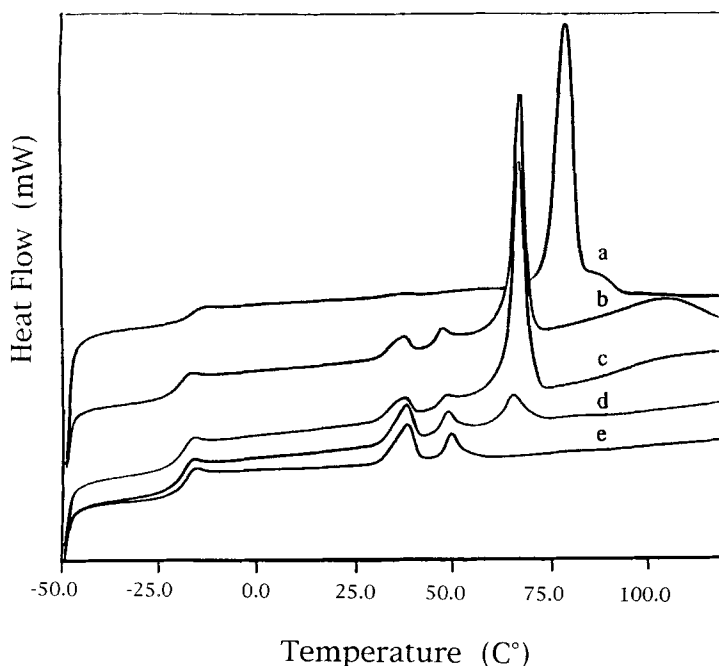
to introduce media molecules for its degradation. If no pathway was formed, the degradation time of PAA would be extended.

The undegraded materials showed a porous structure (Figure 4a) and this structure changes depending on the composition and degradation of the blend. The water molecules penetrate easily into the porous matrices. The hydrolysis then proceeds at the external surface and internal surface of the matrix. Water molecules may more easily penetrate into the matrix that has more porous structure. It appears that the degraded part disappeared leaving crystal-like outgrowths emerging from the matrix (Figure 8a). By looking at the degradation of copolymers of TMC and  $\epsilon$ -Caprolactone by DSC [11] the amorphous regions of materials is degraded first causing the proportion of crystalline material to increase. This phenomenon can be explained by the usually taken assumption that degradation takes place first or/and faster in the amorphous phase of the semicrystalline polymers [21-23]. The sample gradually shrink as it degrades. After 600 hours, most of the blend had collapsed and the remaining sample had formed a fine network (Figure 8b). The holes and pores probably were formed mainly by the degradation of PAA, which supported by the analysis of the sample composition. The surface became progressively more



**Figure 8.** SEM micrographs from selected blend samples containing 50% PTMC (a) after 95 hours of incubation, containing ca. 88% PTMC, surface; (b) after 600 hours of incubation, containing ca. 98% PTMC, surface.





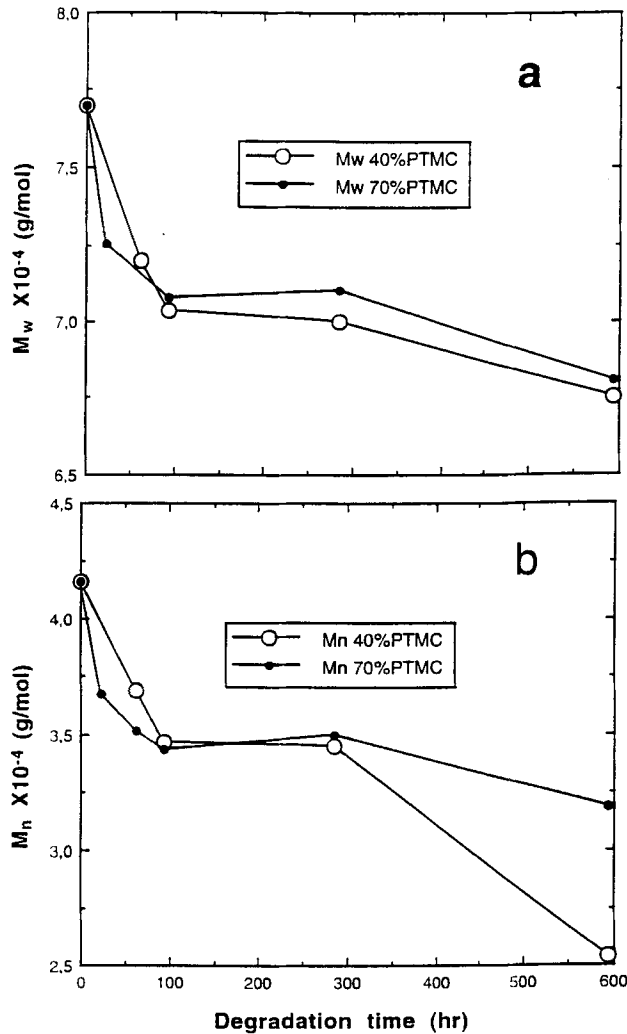
**Figure 9.** Melting endotherms for PTMC/PAA blends as a function of degradation time recorded by DSC at the second heating scan. (a) non-degraded; (b) after 24 hours of degradation; (c) after 95 hours of degradation; (d) after 430 hours of degradation; (e) after 600 hours of degradation.

rough. Langer and his co-workers have shown that the hydrophobicity and the crystallinity of the polymer are the most important factors controlling the type of erosion taking place [24]. Both high hydrophobicity and high crystallinity prevent water diffusion into the polymer bulk and thus prevent bulk erosion. The aliphatic PTMC exhibits a hydrophobic backbone and aliphatic PAA exhibits high crystallinity that is usually favorable of surface erosion. However, thick dispersion and heterogeneity of the mixture from PTMC/PAA blends provided a potential access to bulk erosion.

In the DSC thermogram, a sharp endotherm was observed for PAA (Figure 9b-d) at 67°C, corresponding to the melting of the crystalline regions of the polymer more than 24 hours of degradation. DSC results show that PAA crystalline component in the blends degrades, suggested by its changes of crystalline area. Indeed, after an adequate period of degradation (depending on the relative concentration of both polymers), the non-degraded material, which initially had only one

melting peak (Figure 9a), began to display double or triple peaks and its PAA peak shifted to lower temperature during exposure to the phosphate buffer solution at 37°C. The other two melting points arose indicating the formation of two new types of crystalline phases (Figure 9b-e). Polymer chain scission occurred and resulted in depression of the melting peaks ( $T_m$ ). The peaks at 37°C and 48°C tend to increase as the samples degrade (Figure 9b-e). This implies that the crystalline area in PTMC with lower molecular weight and a possible new crystalline area from degradation of original PTMC and PAA increase during degradation. PTMC with higher molecular weights is an amorphous polymer, but for PTMC with lower molecular weights up to approximate 15,000 the polymer chains are able to crystallize within a week with a resulting melting point of 38.5°C measured by DSC [10]. The crystallization is probably an effect of a reorganization of the chains facilitated by degradation. After 600 hours of degradation, the peak at 67°C disappears completely, suggesting that the crystalline part of PAA in the blend degraded completely. As large amounts of degradation products are set free into the incubation solution, it is seemed likely that those new peaks originate from the components degraded noncompletely, i.e. PTMC oligomers, or a combination of degraded fraction and part of undegraded blend. This was supported by the depression in molecular weight of PTMC in the blends, GC-MS analysis of degradation products for no 1,3-propanediol detected in degradation media as well as the composition analysis for degraded samples.

The changes in molecular weight for the polymer samples during degradation give a good indication for the degradation rate and the material deterioration [11]. The molecular weight of PTMC in the blend obviously decreases as the degradation proceeds (Figure 10), e.g. for the samples of 70% PTMC,  $M_n$  drops 24%,  $M_w$  drops 12%, and polydispersity (PD) of PTMC in the blend increases 16% after 25 days of degradation. For the samples of 40% PTMC,  $M_n$  drops 39%,  $M_w$  drops 12%, and PD increases 44% after the same period of degradation. Compared to the degradation of PTMC homopolymers under the same conditions [11], obviously for homopolymer of PTMC the molecular weight decrease is very slow starting after 600 days of incubation. For the random copolymer series of TMC and  $\epsilon$ -caprolactone,  $M_n$  drops 78% and  $M_w$  drops 67% and PD increases from 1.72 to 2.65 (54%) during 459 days [11]. The rapid decrease in molecular weight for PTMC in the blend may be attributed to the effect of PAA for its mixing and partial compatibility with PTMC or its plasticization to PTMC, as well as the degradation of PAA. The degradation of PAA in bulk of matrix could create an acidic micro-environment, which makes it possible that PTMC in bulk degraded. And the



**Figure 10.**  $M_w$  (a) and  $M_n$  (b) of blends containing 40% and 70% PTMC respectively as a function of the incubation time.

degradation of PAA continuous phase could form a pathway for the medium molecules.

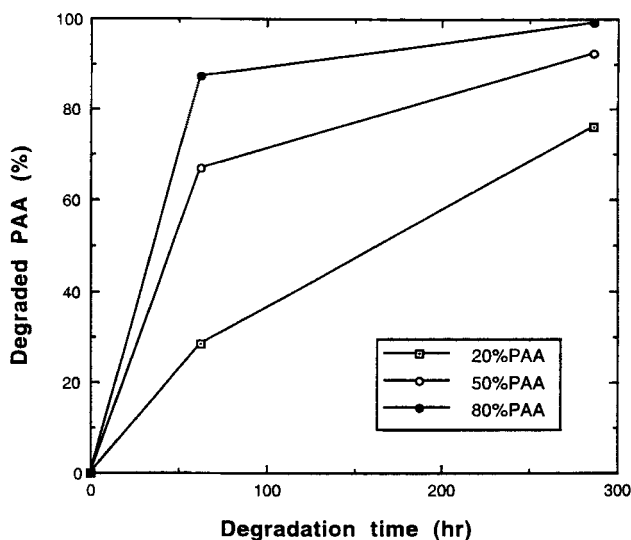
Molecular weight distribution produces an absolute indicator that the polymer has undergone scission [25]. The result indicates that the filling of PAA oligomers, which acted as a fast-degraded plasticizer and resulted in an acidic environment, to PTMC could speed up the degradation of PTMC in phosphate buffer solution. In addition, through physical blending or mixing of a plasticizer into

a polymer, a more convenient, lower cost and composition-controlled method to combine two components with different degradation properties, one could be expected to change the original degradation properties of components.

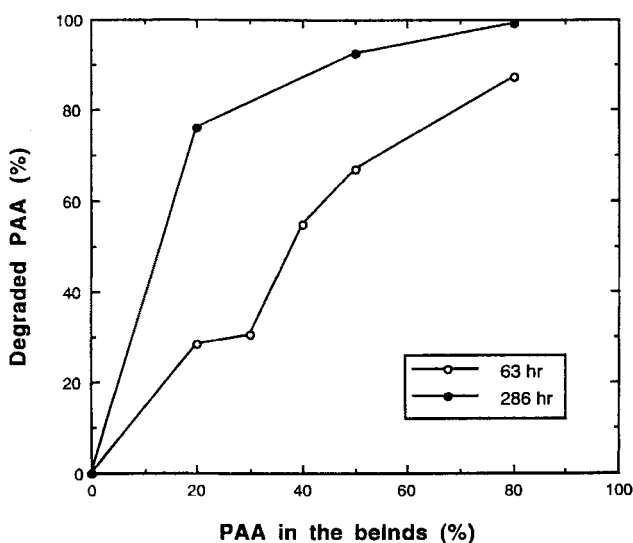
The mechanism of degradation for PTMC and PAA is predominantly a hydrolytic cleavage of the labile bonds such as anhydride and ester bonds, which results in a larger fraction of lower molecular weight chains, oligomers and some harmless ultimate degradation products corresponding to the repeating units of the corresponding polymers, i.e. 1,3-propanediol, CO<sub>2</sub>, and adipic acid. From the GC-MS results, adipic acid was detected and 1,3-propanediol was not detected in the buffer solution used for degradation. So the decrease in molecular weight of PTMC in the blends can be attributed to the formation of PTMC oligomers. This result also clarifies the appearance of the new melting peaks on DSC curves (Figure 9). Because low molecular weight PTMC are semicrystalline. Moreover, the analysis for degraded PAA from GC-MS and that from SEC were correlated with each other.

The degraded PAA (%) was estimated by the ratio of adipic acid in the buffer solution detected by GC-MS to original PAA weight in the blends. The degraded PAA as a function of time and the composition of the blends (Figures 11 and 12). Incubation media would affect the PAA on the surface first and the first degraded component is PAA in the mixtures. The PAA molecules in bulk needs pathway to contact medium molecules and they would be gradually affected by medium molecules after the pathways were formed. The results in Figures 11 and 12 indicated that the degradation rate of PAA in the blends is directly proportional to the content of PAA in the blends, suggested that the diffusion rate of water molecules into the blend matrix and that of adipic acid molecules from the degradation into the degradation media were affected by the content of PAA in the blends. Of course, the presence of a continuous PAA phase will ensure rapid access of media molecules to the PAA in the bulk, meanwhile, provide an acidic environment to PTMC in bulk and extended exposure to buffer solution, due to adipic acid released from degraded PAA. The results also supported that the weight loss of PAA was contributed to the most part of sample weight loss.

Degradation kinetics: the degradation rate can be expressed by the rate constant  $k$  which can be calculated from the number average molecular weight  $M_n$  using expressions derived from a kinetic model valid for chain cleavage by Pitt and Gu [26]. Degradation kinetics were studied and presumed to follow an uncatalyzed or autocatalyzed hydrolysis mechanism according to the work of Pitt and Gu. In this model an uncatalyzed hydrolysis follows the equation:



**Figure 11.** Degraded PAA (%), detected adipic acid from GC-MS analysis to the original PAA weight in the blends, as a function of degradation time.



**Figure 12.** Degraded PAA (%), detected adipic acid from GC-MS analysis to the original PAA weight in the blends, as a function of PAA contents (%) in the blends after 63 and 286 hours of degradation.

$$1/M_n = 1/M_{n0} + k_1 t \quad (1)$$

If the hydrolysis is autocatalyzed the equation changes to:

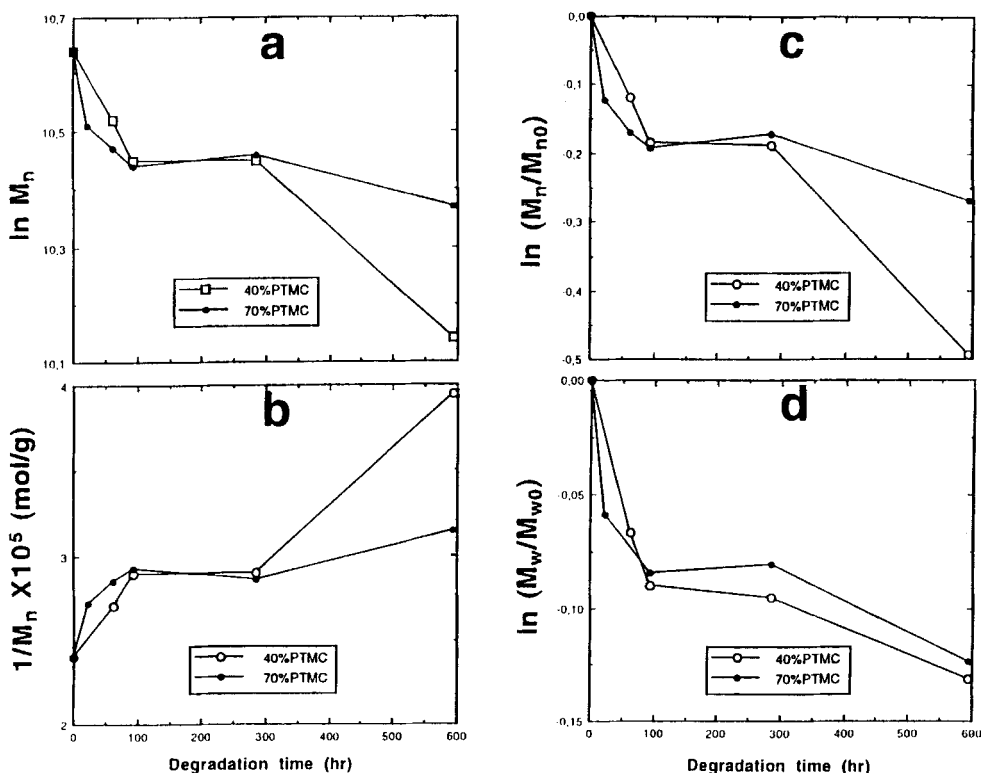
$$\ln(M_n) = \ln(M_{n0}) - k_2 t \quad (2)$$

Two equations are derived for the autocatalyzed and the uncatalyzed hydrolysis reaction, where  $M_{n0}$  is the number average molecular weight before hydrolysis,  $k_1$  and  $k_2$  are the rate constants, and  $t$  is the degradation time. During the hydrolysis of ester and anhydride functionalities carboxylic and hydroxyl end groups and  $\text{CO}_2$  are generally generated, which can further catalyze the hydrolysis due to their existence [27]. Plotting the experimental data from the degradation study according to equations (1) and (2) the prevailing mechanism can be elucidated assuming the degradation occurs under one of these mechanisms above. Figure 13a-b shows the resulting plots. However, no clear conclusions can be drawn regarding the mechanism. It seems impossible to make a linear fit of the data to obtain the values of  $k_1$  and  $k_2$  that describe the rate of hydrolysis.

Taking them into account, we cannot say that the prevailing mechanism is one or the other but possibly both at the same time or different mechanisms in different degradation stages or any other mechanism. The approach of Pitt and Gu for kinetic evaluation is probably limited by some assumptions not applying to our system. It is important to study further the kinetic aspects in order to better understanding the degradation mechanism of different systems.

Plotting  $M_n$ ,  $M_w$  (Figure 10a-b),  $\ln(M_n/M_{n0})$  and  $\ln(M_w/M_{w0})$  (Figure 13c-d) to degradation time, it is difficult to find any linear correlation between these data and the degradation time. Thus, PTMC/PAA blend system degraded not as a simple zero-order or a first-order kinetic mechanism.

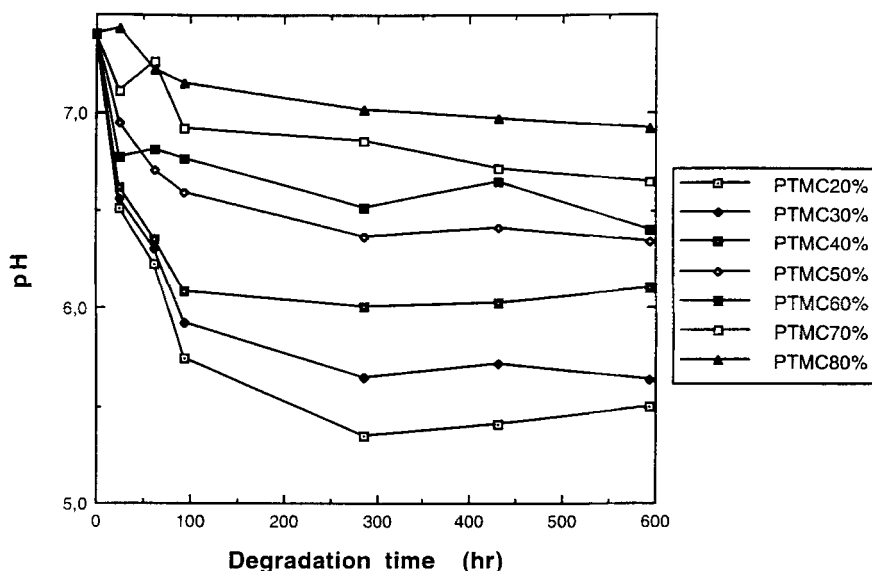
In the majority of blends, the rate of blend degradation was between the degradation rates of the component polymers [20]. The pH values of the incubation media change depending on the composition of the blends (Figure 14). pH value decreases with degradation time. When the decreases come close to certain degradation time the changes become smaller and smaller. After 300 hours of degradation, pH values of the incubation buffer show little change, which is in accordance with the weight loss of the corresponding samples (Figure 5). The results indicated again that the weight loss of the samples mainly comes from the weight loss of PAA in the blends due to less than 10% of PAA left in the samples after 300 hours of incubation.



**Figure 13.** Degradation kinetics expressed by  $\ln M_n$  (a),  $1/M_n$  (b),  $\ln(M_n/M_{n0})$  (c) and  $\ln(M_w/M_{w0})$  (d) as a function of degradation time for the blends containing 40% and 70% PTMC respectively.

Our previous work showed that the pH of PTMC series are almost unchanged ( $M_n > 57,000$ ) due to no acidic end-products are formed in the degradation media over one year [11]. The pH of the solution from PAA series drops drastically (from 7.4 to 4.0 within 40 hours of degradation) due to the large amount of adipic acid that is formed during the rapid degradation and exceeding the buffer capacity [11,15, 28 and 29]. As compared with the previous results, the changes in pH value in this case exist between PTMC series and PAA series (from 7.4 to 5.3 within 300 days). It seems that the degradation rate may be adjusted by the composition of the blends and degradation time.

The immediate application that one may find for these polymer mixtures is the ability to alter the degradation and drug release rate from degradable polymers.



**Figure 14.** Evolution of pH values for the PTMC/PAA blend series incubated in the buffer solutions, 37°C, as a function of the incubation time.

For this application, a stable uniform mixture might be sufficient, and a blending in the molecular level is not necessary [5]. Future studies will concentrate on the evaluation of polymer mixtures that presented some degree of miscibility, and on understanding the incompatibility of polymers containing anhydride and ester segments.

## CONCLUSIONS

1. DSC results show that the  $T_g$  of PTMC and  $T_m$  of PAA in the blend are lower than those in the homopolymers.  $T_g$  and  $T_m$  of the blends are functions of the molecular weight of PTMC. Uniform and translucent films with elasticity could be formed. The blend of PTMC and PAA is heterogeneous microscopically and uniform macroscopically. PTMC and PAA are partially compatible with each other.

2. SEM photographs show that a thick dispersion occurs in the blends which changes with the composition and degradation of the blends. The changes in the thermal properties and in morphology showed a phase separation existing in the blends.



3. DSC confirms that after an adequate period of degradation, the formation of new crystalline phases and the disappearance of the old one. At last the peak at 67°C corresponding to PAA crystalline disappeared completely, indicating that PAA crystal component in the blends degrades completely after 25 days of degradation. The composition analysis for degraded samples showed that the weight loss of the samples resulted mainly from PAA weight loss.

4. The molecular weight of PTMC in the blend obviously decreases as the degradation proceeds and polydispersity of PTMC increases. The results confirmed that the filling of PAA oligomers, which acted as a fast-degraded plasticizer and resulted in an acidic environment, to PTMC could speed up the degradation of PTMC in phosphate buffer solution. GC-MS and DSC suggested that the depression in molecular weight is attributed to the formation of PTMC oligomers from degradation. The degradation of PTMC would increase with the increasing of media acidity.

5. The degradation rate of PAA in the blends is directly proportional to the content of PAA in the blends.

6. The degradation proceeded in neither a simple uncatalyzed nor autocatalyzed hydrolysis mechanism and did not obey zero-order and first-order kinetic mechanisms.

7. Degradation rate and pH of the degradation media change depending on the composition of the blends and degradation time.

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