

Polymer Blends Based on Poly(vinyl chloride) and Biodegradable Aliphatic–Aromatic Copolyester

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ABSTRACT: Blends of poly(vinyl chloride) (PVC) and biodegradable aliphatic–aromatic copolyester (AAC) were prepared, and their physical, thermal, and mechanical properties were studied. Biodegradation in the presence of the lipases of *Rhizopus arrhizus* or *Candida cylindracea* was monitored as well. The physical properties of the blends, such as density and softening temperature, were between those of each component. Differential scanning calorimetry measurements showed that the blend components were completely amorphous and miscible. Obviously, PVC suppressed the crystallization of the partially crystalline copolyester.

AAC was the thermally more stable component, and it seemed to improve the thermooxidative stability of PVC in the blends. The lipases of *R. arrhizus* and *C. cylindracea* no doubt catalyzed the ester hydrolysis of AAC, although the PVC matrix limited the rate and extent of the hydrolysis. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1002–1008, 2008

Key words: degradation; mechanical properties; poly(vinyl chloride)PVC; polyesters; thermogravimetric analysis (TGA)

INTRODUCTION

Many synthetic and naturally occurring polymers have limited or even no applications by themselves. However, when they are mixed with a wide spectra of additives, useful materials have been developed. Similarly, the blending of two or more polymers is a more convenient way of developing new plastic materials. Developing a blend of existing polymers is more cost-effective and less time consuming than polymerizing a new polymer for a particular product. Polymer blends constitute approximately 36 wt % of total polymer consumption, and this number continues to increase.¹ Depending on the ratio of the components, materials with different properties can be obtained. Such an example is poly(vinyl chloride) (PVC), which has versatile applications due to its wide variety of blends and mixtures. Recent investigations have been and future demands will be focused on the search for nontoxic plasticizers and environmentally friendly stabilizer systems. Also, the further improvement of other properties of PVC to make engineering plastics from a commodity will be important in the future. An interesting article con-

cerning PVC was published recently by Braun.² From an ecological point of view, the main disadvantage of PVC and other synthetic plastics is their nondegradability in the environment. Generally, the resistance of plastics is caused by two factors: (1) the low surface area and relative impermeability of plastic objects and (2) the high molecular mass of plastic.³ However, degradation is not always desirable due to the potential release of toxic compounds. Efforts have been made toward decreasing the total volume of plastic waste by the addition of some biodegradable components. The easiest method is the incorporation of starch or cellulose in the polymer matrix, and some examples of this include low-density polyethylene filled with starch^{4,5} for packaging purposes and PVC filled with cellulose.⁶ After composting, the mechanical properties of plastic materials are poorer, and these materials can be easily disintegrated into smaller pieces. On the other hand, biodegradable polyesters, such as poly(ϵ -caprolactone), poly(3-hydroxybutyrate), and polylactide, and different aliphatic–aromatic copolyesters (AACs), derived either from renewable resources or petrochemicals, are often expensive, and therefore, their applications are limited. By blending them with conventional thermoplastics, one can produce low-cost materials with improved properties. The blending of a thermoplastic resin with a biodegradable one must produce a dispersion so that after the disintegration of the biodegradable part, the thermoplastic powder will not contaminate the environment.¹ Investiga-

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TABLE I
Physical Properties of the Plastics Used to Prepare the Blends

AAC		PVC	
Density at 20°C (g/cm ³)	1.25	K_{value}	58 ± 1
Number-average molecular weight	20,030	Glass transition (°C)	79
Glass transition (°C)	-35	Chlorine content (%)	56
Melting point (°C)	95		

tions have been performed on various combinations of biodegradable polyesters with poly(vinyl acetate),⁷ polystyrene,^{8,9} polycarbonate,¹⁰ and linear low-density polyethylene.¹¹

In this study, we investigated the thermal and mechanical properties and the biodegradation of PVC/AAC blend sheets. It was of interest to us to study whether AAC could be a substitute for any common modifier for PVC. The blends of those two polymers are completely miscible due to the specific interactions of the carbonyl oxygen in AAC with the α -hydrogen in PVC, as previously detected by FTIR and differential scanning calorimetry (DSC) measurements of PVC/AAC blends without additives.¹² Published investigations by other authors have shown that the blends of AAC and aliphatic polyesters are partially miscible,¹³ and AAC and polystyrene were considered as relatively compatible.⁸

EXPERIMENTAL

Materials and blend preparation

The PVC we used was a commercially available, suspension-grade Ongrovil S-5258 ($K_{\text{value}} = 58 \pm 1$, chlorine content = 56%) supplied by Borsod Chemical (Kazincbarcika, Hungary). AAC was a commercial copolymer of 1,4-butandiol and adipic and terephthalic acids, which was partially crystalline (number-average molecular weight = 20,300, as determined by the end-group analysis method)¹⁴ and was supplied by Eastman Chemical Co. (Kingsport, TN) Both resins were used as received, and some of their physical properties are compiled in Table I. Although the ratio of the monomers in the AAC copolymer was not available, on the basis of

the melting temperature and glass-transition temperature (T_g), we assumed that the molar ratio of terephthalic acid and adipic acid was about 40 : 60.^{15,16}

Polymer blends containing 0–30 mass % AAC were prepared on laboratory roller mill at 135–140°C and were then hot-pressed at 170°C. Processing additives were also added (Table II). The resulting sheets were clear and transparent. Polymer blend sheets with more than 30% AAC and the AAC alone were too sticky, and it was impossible to prepare them properly on a laboratory roller mill.

Density determination

The densities of the samples were determined according to ISO 1183 with a density gradient column system 6001/000 (CEAST Societá per Azzioni, Italy). The specimen was placed in a density gradient column. The column contained a water–calcium nitrate solution. The density of the specimen was determined by the vertical location of the specimen in the column.

Vicat softening temperature determination

Vicat softening temperatures were determined according to ISO 306 with a HDT 3 Vicat P/N 6911/000 (CEAST Societá per Azzioni).

Mechanical testing

Tensile strength and elongation on break were tested according to ISO 527-3 with an Instron 4302 universal testing machine (Instron, Bucks, UK) at crosshead speed of 20 mm/min. The sheet thickness was 1 mm.

Thermogravimetric analysis

Thermal degradation of the samples was performed on a TGS-2 thermobalance (PerkinElmer, Waltham, MA) in the temperature range 50–650°C at a heating rate of 10°C/min in nitrogen and in synthetic air (Messer, Austria). From the thermogravimetry (TG) and differential thermogravimetry (DTG) curves, the temperature of 5% mass loss ($T_{5\%}$) and the temperature at the maximum degradation rate of the first step (T_{max}) were extrapolated.

TABLE II
Processing Additives Contained in the PVC/AAC Blends

Additive	Trade name and supplier	Quantity (wt %)
Processing aid	Paraloid K-120 N, Rohm & Haas (Philadelphia, PA)	1.0
Heat stabilizer	Irgastab 17 MOK, Ciba-Geigy (Basel, Switzerland)	1.0
Heat costabilizer	Irgaplast 39, Ciba-Geigy (Basel, Switzerland)	1.0
Internal lubricant	Advalube 1060 L, Rohm & Haas (Philadelphia, PA)	0.5
External lubricant	Advalube 2101 E, Rohm & Haas (Philadelphia, PA)	0.3

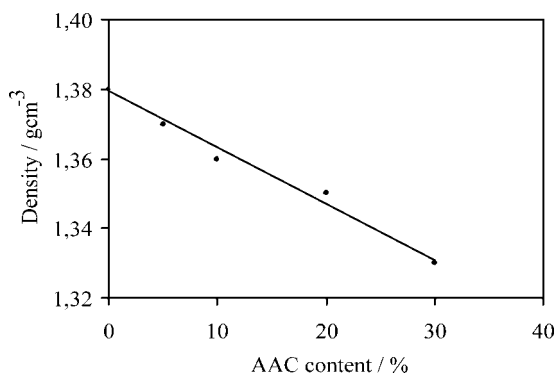


Figure 1 Density of the PVC/AAC blends.

DSC

DSC was performed on DSC 2910 instrument (TA Instruments, New Castle, DE) with a cooler system that used liquid nitrogen. The calorimeter was calibrated with an indium standard.

The procedure consisted heating initially from ambient temperature to 140°C, cooling to -50°C, and reheating to 140°C at heating/cooling rates of 10°C/min. T_g values of the blends were collected from the second heating scan as the temperature when the specific heat reached the half of its total change (midpoint).

Enzymatic degradation

Enzymatic degradation of the samples (3×1 cm, total area = 6 cm², thickness = 0.16 ± 0.01 mm) was performed at 40°C in a 0.1% solution of the lipase of *Rhizopus arrhizus* or *Candida cylindracea* (Fluka, Buchs, Germany) in potassium phosphate buffer (pH = 7.5). The samples were placed in vials containing 10 mL of the solution, removed from the vials after 24 h, washed with distilled water, and dried *in vacuo* to a constant weight. The same samples were returned

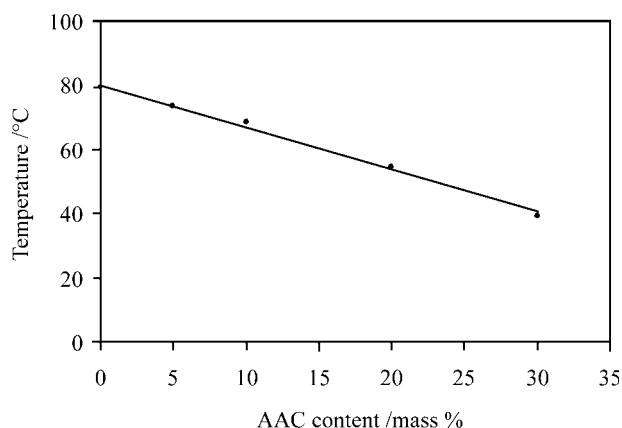


Figure 2 Vicat softening temperature of the PVC/AAC blends.

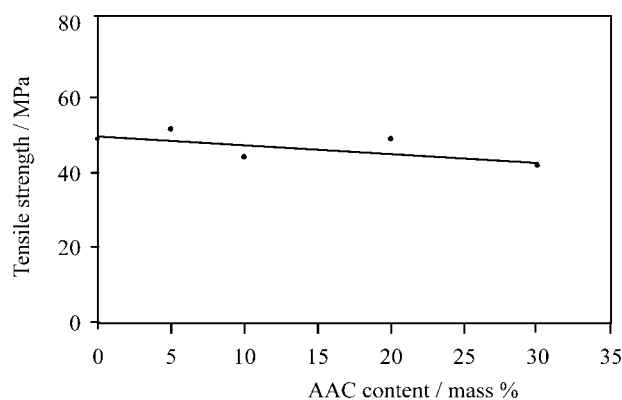


Figure 3 Tensile strength of the PVC/AAC blends.

to vials with fresh enzyme solution for another 24 h. The degradation was monitored for 8 days (192 h). The activity of *R. arrhizus* was 2.2 U/g, and that of *C. cylindracea* was 1.6 U/g. One unit was defined as the amount of enzyme that catalyzed the release of 1 μmol of oleic acid per minute at pH 7.4 and 40°C.

Sheet samples were also immersed in potassium phosphate buffer solution, without enzyme addition, to estimate the noncatalyzed hydrolysis effect alone. The procedure was the same as that described previously.

The weight loss percentage (W_n) was calculated as follows:

$$W_n = [(W_0 - W_t)/W_0] \times 100 \quad (1)$$

where W_0 and W_t are the initial and actual sample weights.

RESULTS AND DISCUSSION

In a previous investigation performed in our laboratory,¹² we found that coprecipitated PVC/AAC blends were completely miscible and that AAC in the blends was amorphous. Those facts were the

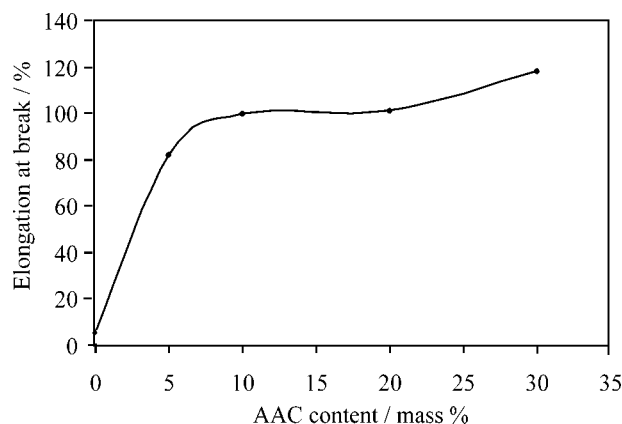


Figure 4 Elongation at break of the PVC/AAC blends.

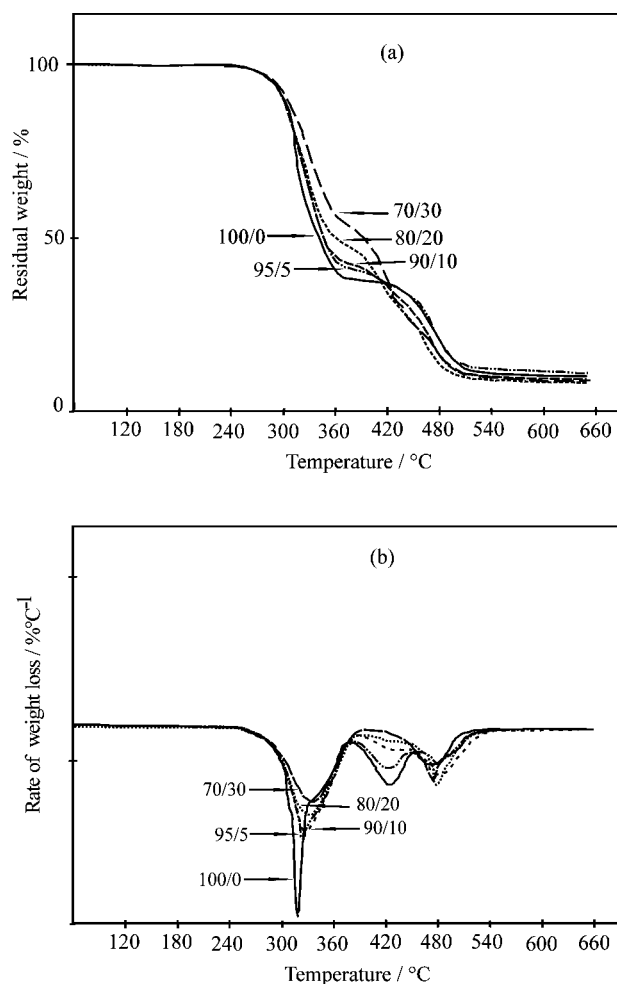


Figure 5 (a) TG and (b) DTG curves of the PVC/AAC blends in nitrogen.

reason we investigated the PVC/AAC blend sheets further. Some physical, mechanical, and thermal properties were determined. Enzymatic degradation was also monitored.

The densities of the PVC/AAC sheets linearly decreased with increasing AAC content, as shown in Figure 1, because of the lower density of AAC.

The Vicat softening temperature also linearly decreased with increasing AAC content (Fig. 2).

The decrease in the softening temperature was the result of the lower softening temperature of AAC in comparison to PVC.

The tensile strengths of the blend sheets were similar to those of PVC (Fig. 3). However, the elongation at break showed an initial jump and then a slow increase with increasing AAC content (Fig. 4). PVC is a stiff and brittle plastic material and needs to be modified with different plasticizers. When AAC was added, the PVC sheets became more flexible, and the tensile strength remained almost unchanged.

The thermal degradation in nitrogen occurred through three main degradation steps (Fig. 5),

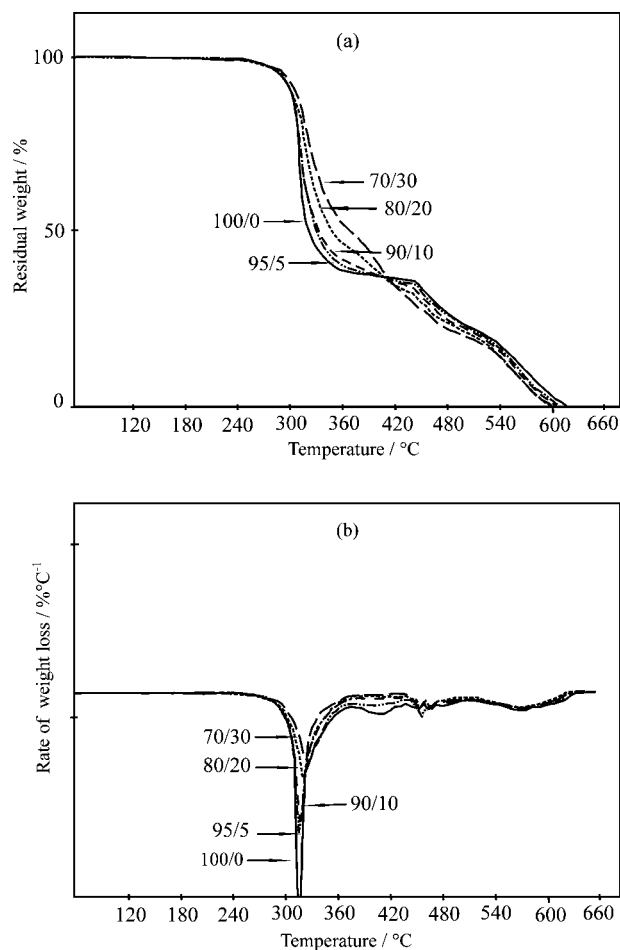


Figure 6 (a) TG and (b) DTG curves of the PVC/AAC blends in air.

whereas the oxidative degradation occurred through a few more steps (Fig. 6) because of the general difference between pyrolysis and oxidative degradation reactions. The first visible mass loss, in both atmospheres, took place at about 250°C. Oxidative degradation up to 650°C was complete, but the pyrolytic

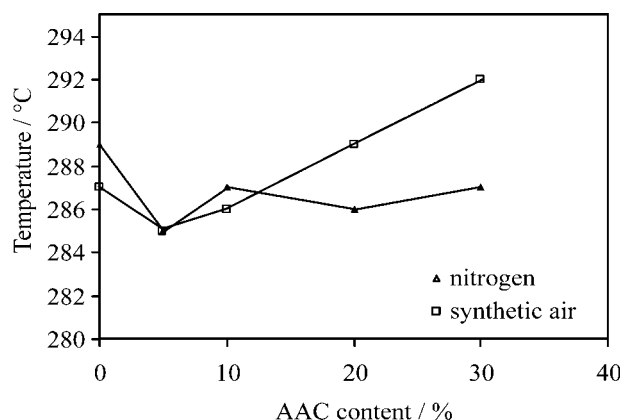


Figure 7 Dependence of $T_{5\%}$ on the AAC content in the blends.

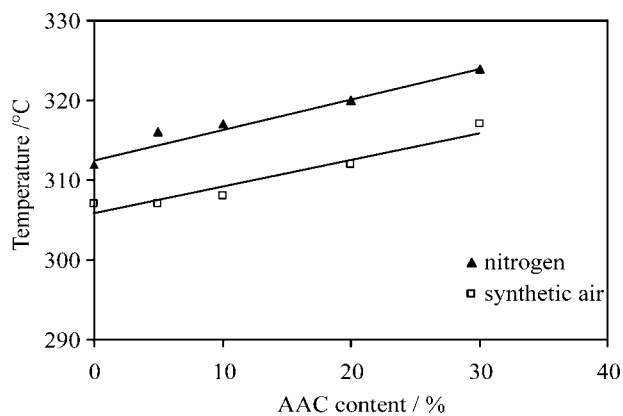


Figure 8 Dependence of T_{\max} on the AAC content in the blends.

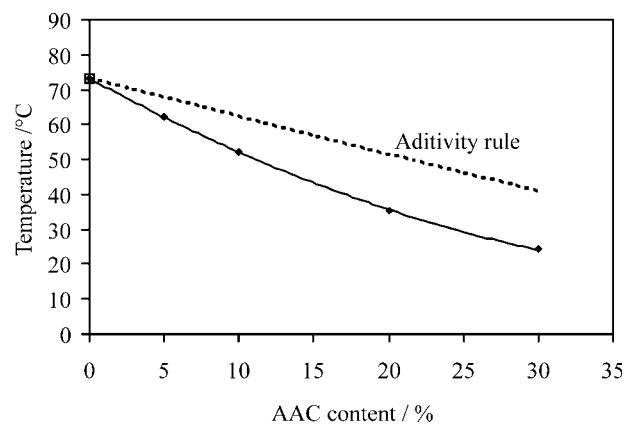


Figure 10 T_g of the PVC/AAC blends.

residue at the same temperature was 10–13%. According to the DTG curves, the degradation rates of the first step in the air were higher, and degradation took place in a narrower temperature range than in nitrogen. $T_{5\%}$ was taken as the indicator of initial blend degradation in the different atmospheres. PVC alone was more stable in the inert atmosphere than in the oxidative one. $T_{5\%}$ of the blends with AAC in nitrogen was below $T_{5\%}$ of PVC (Fig. 7). The stability of the blends with 20 and 30% AAC in air was improved and was even higher than that of PVC in nitrogen. The T_{\max} values for all compositions were lower in air, too (Fig. 8), and, in both cases, was shifted to higher temperature values with increasing AAC content. The influence of unconsumed heat stabilizers and costabilizers added to prevent thermal degradation during sample processing on the overall stability of the blends should not be neglected.

DSC measurements showed only one transition, that is, the glass transition between the glass transitions of the components (Fig. 9). T_g decreased from

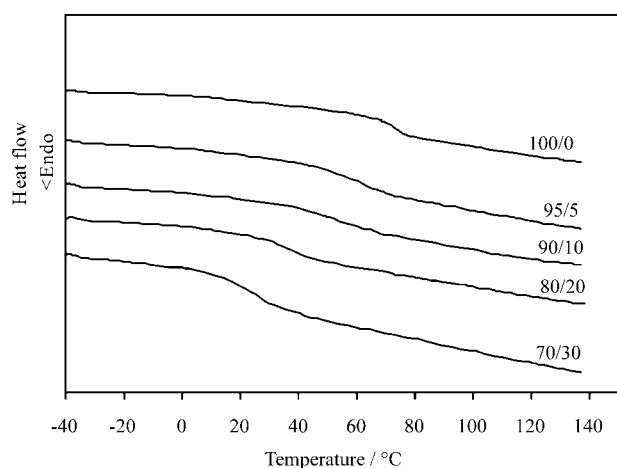


Figure 9 DSC curves of the PVC/AAC blends.

73°C for the 100/0 PVC/AAC composition to 24°C for the 70/30 composition (Fig. 10). Deviations from the rule of mixtures were negative, which is characteristic of miscible blends, with miscibility achieved due to specific interactions. The decrease in T_g of the blends was not influenced only by AAC. It was proven that T_g of PVC decreased in the presence of other miscible additives, such as thermal stabilizers.¹⁷ With regard to the neat polymer, AAC in the blends was no longer partially crystalline but was completely amorphous, and we supposed that intermixing of the polymers at a molecular level occurred.

Recent investigations have pointed out that the biodegradation behavior of AACs can be explained by their solid-state structure and can be well described by the concept of chain mobility.^{16,18} As a measure of this mobility, the difference between the melting point and the temperature of degradation was used. The susceptibility to an enzymatic attack is higher when this difference is reduced. In the amorphous region, chain mobility is much higher than in the crystalline region, and it was realistic to expect that amorphous AAC in the blend with PVC would be more susceptible to degradation by lipase-like enzymes.

In a polymer chain of random AACs, four kinds of different bonds can be distinguished: ester bonds between butandiole and two aromatic acids, other ester bonds between butandiole and two aliphatic acids, and two kinds of ester bonds connecting butandiole and aliphatic and aromatic parts of the copolymer.¹⁹ Lipaselike enzymes will attack only aliphatic–aliphatic esters bonds, possibly because of the steric hindrance for bonds near terephthalic acid. If a length of aromatic chain segments is varied, copolymers with different thermal properties and different biodegradation abilities can be obtained. Some results have demonstrated that it is not the length of the aliphatic domain but that of aromatic chain seg-

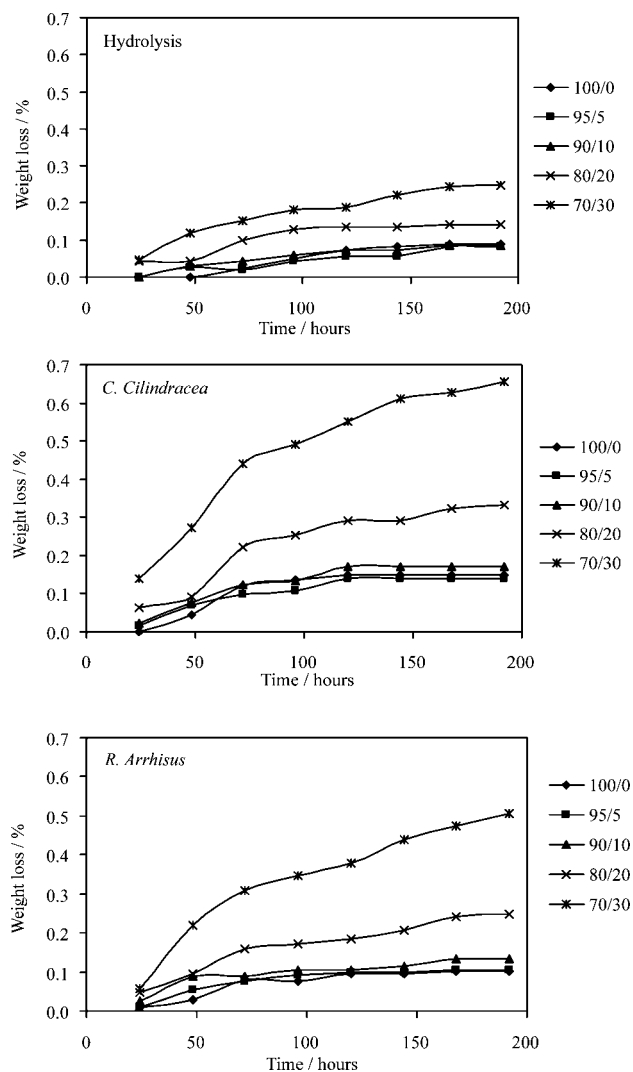


Figure 11 Hydrolytic and enzyme-catalyzed hydrolytic degradation of the PVC/AAC blends.

ments that determines the degradation rate of the copolymers.¹⁹ Furthermore, lipases need a hydrophobic surface to be activated to catalyze ester bond cleavage.

The enzyme-catalyzed degradation of PVC/AAC blends was performed in the presence of the lipases of *R. arrhisus* and *C. cilindracea*, and the percentage weight loss per unit surface area was calculated.

Noncatalyzed hydrolytic weight loss increased with time and AAC content as well (Fig. 11). In the PVC/AAC blends, the hydrolysis of added lubricants, which were fatty acids or fatty acid esters in nature, was assumed, and this explained certain weight loss in the blends without AAC. With the addition of an enzyme, weight loss upon hydrolysis was doubled. For the blends with 0–10% AAC, enzymatic weight loss was less than 0.35%. A relatively higher enzymatic weight loss was observed in the 80/20 PVC/AAC blend and especially in the 70/30 PVC/AAC blend, and enzymatic weight loss was the fastest during first 3 days. In the blends with up to 10% AAC, enzymatic hydrolysis was retarded after 7 days of incubation, perhaps because of the disappearance of the AAC component and other hydrolysable components from the surface of the blends. Starting transparent sheets became more turbid with degradation progression of both noncatalyzed and enzyme-catalyzed hydrolysis. The turbidity of the enzyme-degraded samples was more pronounced. With regard to the enzyme species, the PVC/AAC blends were more susceptible to the hydrolysis in the presence of *C. cilindracea* lipase rather than *R. arrhisus* lipase. To estimate the enzyme contribution to hydrolysis, the normalized weight loss of PVC/AAC blends in the buffer was subtracted from the normalized weight loss in the enzyme solutions, and the results are presented in Tables III and IV. On the basis of those results, we observed that weight loss in the 100/0 and 95/5 blends reached the maximum after 72 h and then decreased. We assumed that in those blends, after the consumption of a low content of biodegradable components, noncatalyzed hydrolysis prevailed. In the blends with 10, 20, and 30% AAC, enzymatic hydrolysis was dominant because of the higher content of AAC and consecutively longer time necessary for total enzymatic hydrolysis of AAC on the surface of the blend sheets.

CONCLUSIONS

These investigations showed that PVC/AAC blend sheets prepared in laboratory on two-roll mill were transparent with densities and softening tempera-

TABLE III
Weight Losses of the PVC/AAC Blends in the Presence of the Lipase of *R. arrhisus* Corrected for Weight Loss on Hydrolysis

PVC/AAC	Time (h)							
	24	48	72	96	120	144	168	192
100/0	0.009	0.028	0.056	0.024	0.020	0.013	0.015	0.015
95/5	0.008	0.025	0.055	0.049	0.043	0.043	0.022	0.022
90/10	0.027	0.060	0.045	0.048	0.033	0.042	0.046	0.046
80/20	0.005	0.054	0.060	0.044	0.051	0.072	0.100	0.107
70/30	0.011	0.101	0.155	0.165	0.192	0.219	0.229	0.257

TABLE IV
Weight Losses of the PVC/AAC Blends in the Presence of the Lipase of *C. cylindracea*
Corrected for Weight Loss on Hydrolysis

PVC/AAC	Time (h)							
	24	48	72	96	120	144	168	192
100/0	0.000	0.044	0.099	0.084	0.076	0.069	0.062	0.062
95/5	0.015	0.041	0.078	0.065	0.082	0.082	0.054	0.054
90/10	0.022	0.048	0.080	0.074	0.098	0.098	0.084	0.084
80/20	0.020	0.048	0.124	0.126	0.157	0.157	0.181	0.189
70/30	0.093	0.153	0.287	0.309	0.365	0.391	0.382	0.407

tures between those of each component. The tensile strength was similar to those of PVC sheets, and the elongation at break was about 20 times higher. Surprisingly, thermogravimetric degradation revealed that 80/20 and 70/30 PVC/AAC blends were initially thermally more stable in an oxidative atmosphere than in an inert atmosphere. It should be of interest to investigate the stabilizing mechanism of AAC or its degradation products on PVC. DSC measurements indicate that the PVC/AAC blends were completely miscible. PVC suppressed the crystallization of AAC; thus, AAC in the blend existed in a stable amorphous state. The amorphous regions were more flexible than the crystalline regions, and it is reasonable to expect better biodegradability from amorphous AAC than from partially crystalline AAC. The enzymatic hydrolysis of AAC in the PVC/AAC blends by the lipases of *R. arrhisus* and *C. cylindracea* was detected, but the blends were also susceptible to common hydrolysis in water. Thus, it is possible to make a PVC blend with a biodegradable component that, after biodegradation, contributes to the mechanical disintegration of the plastic.

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