

Development of Potentially Biodegradable Polyamide-6 and Polyvinyl Alcohol Blends: Physico-Mechanical Properties, Thermal Properties, and Soil Test

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ABSTRACT: Blends of polyamide-6 with 5, 7.5, 10, 15, and 20 wt % of polyvinyl alcohol (PVA) were prepared by the extruding in a corotating twin-screw extruder. The extrudate strands were cut into pellets and injection-molded to make test specimens. These specimens were tested for physico-mechanical properties such as tensile strength, impact strength, density, water absorption, hardness, and thermal characteristics by differential scanning calorimetry, heat distortion temperature (HDT), vicat softening point (VSP), and melt flow index. The prepared blends show enhanced biodegradation, water absorption, and density, but it is ob-

served that the introduction of PVA into the polyamide-6 matrix shows considerable reduction in tensile strength, impact strength, HDT, VSP, and hardness initially, but subsequent addition does not show significant reduction because of the enhanced interaction between amide groups of polyamide-6 and hydroxyl groups of PVA. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2339–2346, 2005

Key words: polyamide; blends; biodegradable; glass transition; miscibility

INTRODUCTION

Biodegradable polymeric materials have attracted much attention in recent years, because of the environmental and pollution problems due to the nondegradable and nondisposable nature of the synthetic thermoplastics in use. Among the synthetic thermoplastics materials, polyamide-6 occupies a prominent place in the engineering thermoplastic family because of its processing range, relative ease with which polyamide-6 can be modified to achieve wide spectrum of properties. Polyamide-6 has been used for many engineering applications because of their high strength, excellent chemical, coefficient of friction, and abrasion resistance. However, polyamide-6 generally resists microbial and enzymatic attacks, which becomes a critical problem to the plastics industries. So, there is a growing demand for environmentally degradable plastics. As a viable alternative, it is intended to make degradable blends of synthetic plastics with degradable polymers. Generally, synthetic thermoplastics are modified with starch^{1–7} or natural fibers^{8–12} to make them environment friendly. But there is not much focus on the use of polyvinyl alcohol (PVA) as biodegradable polymer in modification of synthetic plastics. PVA is a synthetic polyhydroxy polymer, having very

good water absorption and bio-compatibility. PVA is one of the few completely bio-degradable synthetic polymers¹³ available today. PVA is usually synthesized by hydrolysis of polyvinyl acetate and are known to be completely biodegradable. However, PVA as such cannot be used as a plastic, because of its higher water absorption and weak thermal stability. Hence, it is intended to be used as a modifier in polyamide-6 through blending process, because blend preparation is the best and economically viable option to modify the plastics, and this is manifested by growing number of monographs and publications^{14–19} on blends.

With the ongoing interest in hydrophilic/bio-degradable polymers,^{20–24} in the present study, it is proposed to blend polyamide-6 with PVA in different proportions with the objective to make this material as environmental friendly and degradable one.

EXPERIMENTAL

Materials

The plastic raw materials used in this study were polyamide-6 (GELON B28N) with melt flow index (MFI) of 7 g/10 min and density of 1.13 g/cc, and polyvinyl alcohol (PVA) (M_n 1400, 90% hydrolyzed) supplied by M/S. GE Plastics Ltd. and M/S. Poly Chem Ltd., India, respectively. The reagent grade dioctylphthalate (DOP) obtained from the local market was used as a wetting agent for PVA.

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TABLE I
Composition of Polyamide-6 and Polyvinyl Alcohol Blend

S. No	Sample code	Percentage composition by weight	
		Polyamide-6	Polyvinyl alcohol
1	A	100	0.0
2	B	95.0	5.0
3	C	92.5	7.5
4	D	90.0	10.0
5	E	85.0	15.0
6	F	80.0	20.0

Compounding

PVA powder was premixed with 0.5% of its weight of DOP, so as to prevent the segregation of PVA during hopper feeding in twin-screw extruder, then mixed with polyamide-6 materials as per the composition given in Table I in tumbling mixer for 15 min, after predrying in hot air oven at 75°C for 3 h duration, and then melt blended in 17.5 mm diameter corotating twin-screw extruder (HAAKE Rheocord 9000, Germany) having L/D ratio 1 : 18 in the temperature range of 145–195°C at 80 rpm. The extrudate strands were cut into pellets and used for further study.

Testing methods

The test specimens as per ASTM standard specifications were made in ENGEL-80 tons automatic injection-molding machine in the temperature range of 200–245°C and injection pressure at 100 bar. The tensile test was carried out on injection-molded dumb-bell specimens in Universal testing machine (Llyod, UK, Model LR 100K) as per ASTM D 638 standard with cross-head speed of 50 mm/min. The impact test was performed on Izod-Charpy digital Impact tester (ATSFAAR, Italy) as per ASTM D 256 A and B standard. Differential scanning calorimetry (DSC) analysis were carried out in Thermal analyzer 2000 series at the rate of 10°C/min from ambient to 300°C in an inert atmosphere. Heat deflection temperature as per ASTM D 648 and vicat softening point (VSP) as per ASTM D 1525 test methods were carried out in heat distortion temperature (HDT)–VICAT tester (ATS FAAR, Italy, model MP/3). MFI testing was performed on extrudate cut pellets in MFI tester (Devanport, UK, type 7273) at 275°C and 0.325 Kg load as per ASTM D 1238. The sample density was measured for extrudate material as per ATSM D 792. Water absorption was measured for injection-molded discs of 50 mm diameter as per ASTM D 570. Shore A hardness was measured using Durometer (P.S.I Sales Pvt. Ltd., India) as per ASTM D 2240 test method.

Soil burial test

Biodegradability was evaluated by measuring tensile strength at yield for tensile specimens made as per ASTM D 638 (type I) buried in soil. Three inches of shifted soil was placed in a plastic box (15 × 10 × 6.5 in.), which was then lined with a stainless-steel cloth for air passage. Soil was kept moistened at a 30% content with deionized water.^{25,26} The soil burial test period was 60 days. After the soil test, the samples were washed with water and dried to their constant weight in an oven at 40°C. The tensile strength at yield was measured for five specimens in each type and the average is reported.

RESULTS AND DISCUSSION

Tensile strength analysis

Polyamide-6 and PVA blends were prepared as per the composition given in Table I. Figure 1 shows sharp reduction in tensile strength at yield with the addition of 5% PVA, but with further addition of PVA does not show significant reduction in tensile strength. Both PVA and polyamide-6 are linear and crystalline polymers. The initial reduction in tensile strength may be attributed to the variation in phase morphology and hydrophilicity, but, further addition of PVA does not show significant reduction in tensile strength. This may be due to enhanced hydrogen bonding between hydroxyl groups of PVA and amide group of polyamide-6, which will resist and prevent the slippage of molecular chains over the other during stretching in the tensile test. The stress–strain curves of polyamide-6 and PVA blends were shown in Figure 2, in which virgin polamide-6 as well as blends show maximum yields accompanied by the formation of necking and followed by cold drawing. The yield stress for blends decreased with increase in PVA content. The yield stress instability of polymeric materials can be characterized by index of cold draw (ICD), which is defined as the ratio of upper yield stress to lower yield stress.²⁷ The larger the ICD, the sharper or more localized the necking. Figure 3 shows the cold draw index versus PVA content. There is a sharp increase in ICD at 5% PVA, but at 7.5% PVA, there is a sharp decrease and further it steadily increased with increase of PVA. This shows that the necking is localized more with increase in PVA content.

Biodegradability of polyamide-6 and PVA blends

Soil burial test is a traditional way to test samples for degradation because of its similarity to actual conditions of waste disposal. This method will be more effective, compared with enzymatic test, if the samples are buried in suitable climatic conditions and the various populations of microorganisms are involved. The

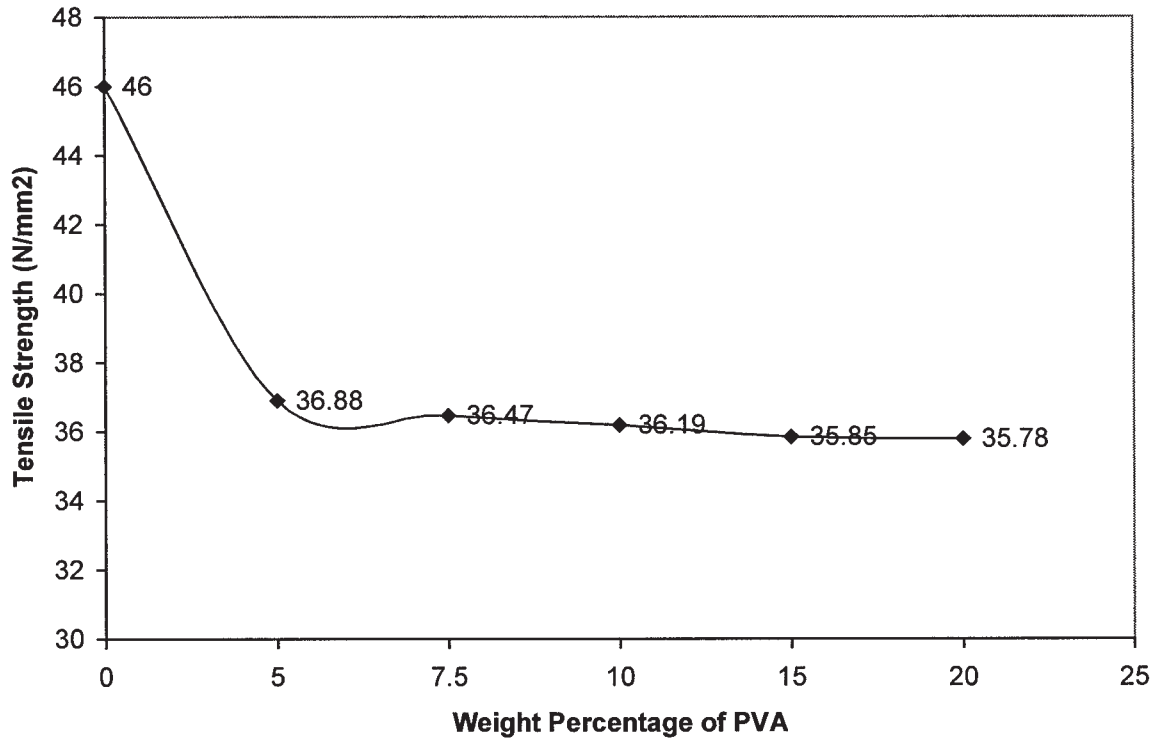


Figure 1 Effect of PVA addition on tensile strength of polyamide-6.

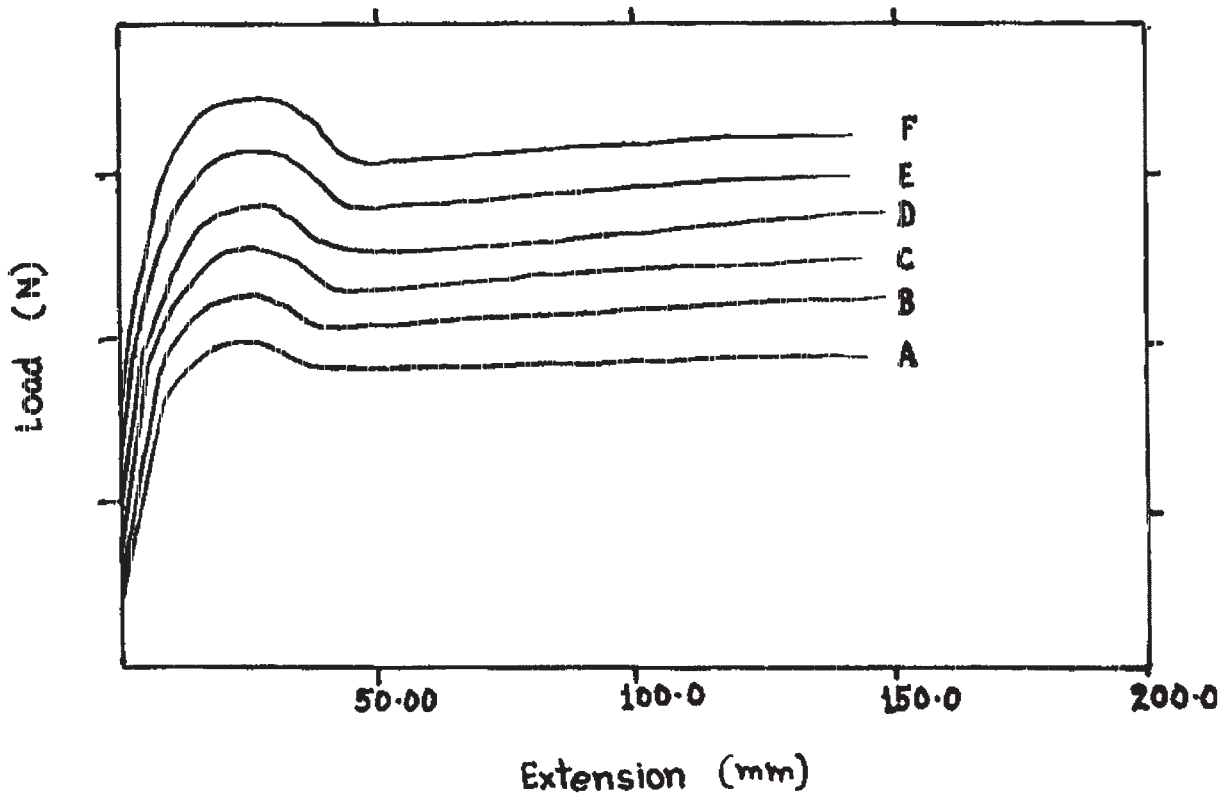


Figure 2 Stress-strain curves of polyamide-6/PVA blends.

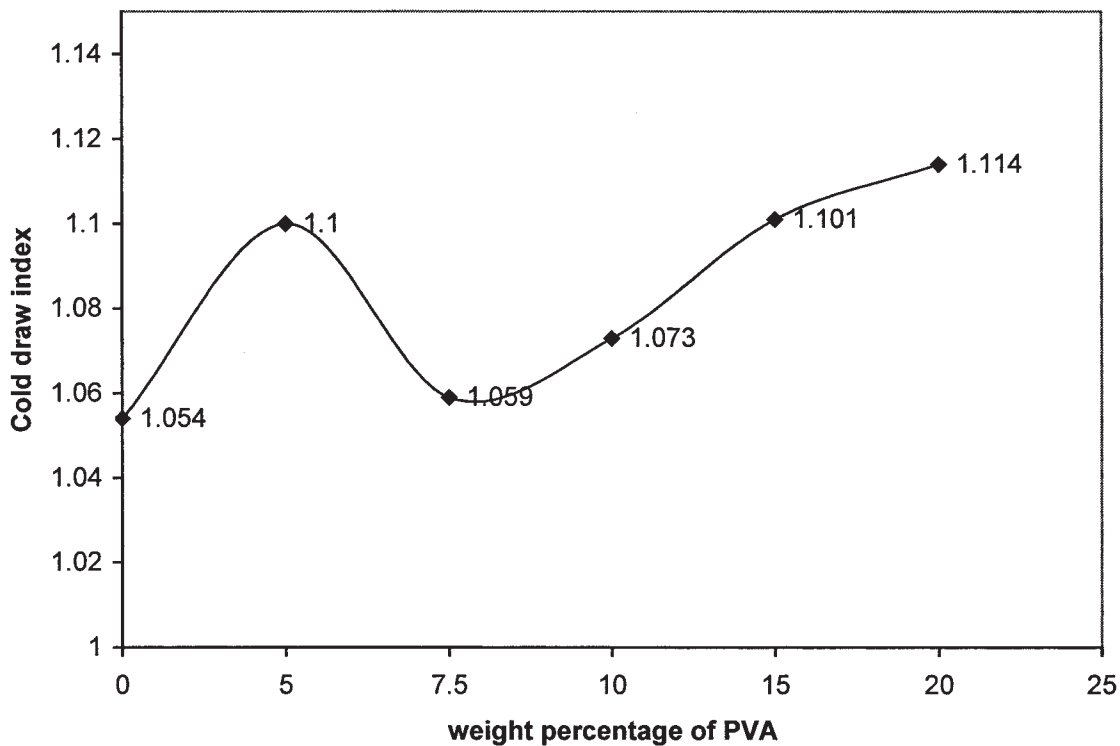


Figure 3 Cold draw index for polymer-6/PVA blends.

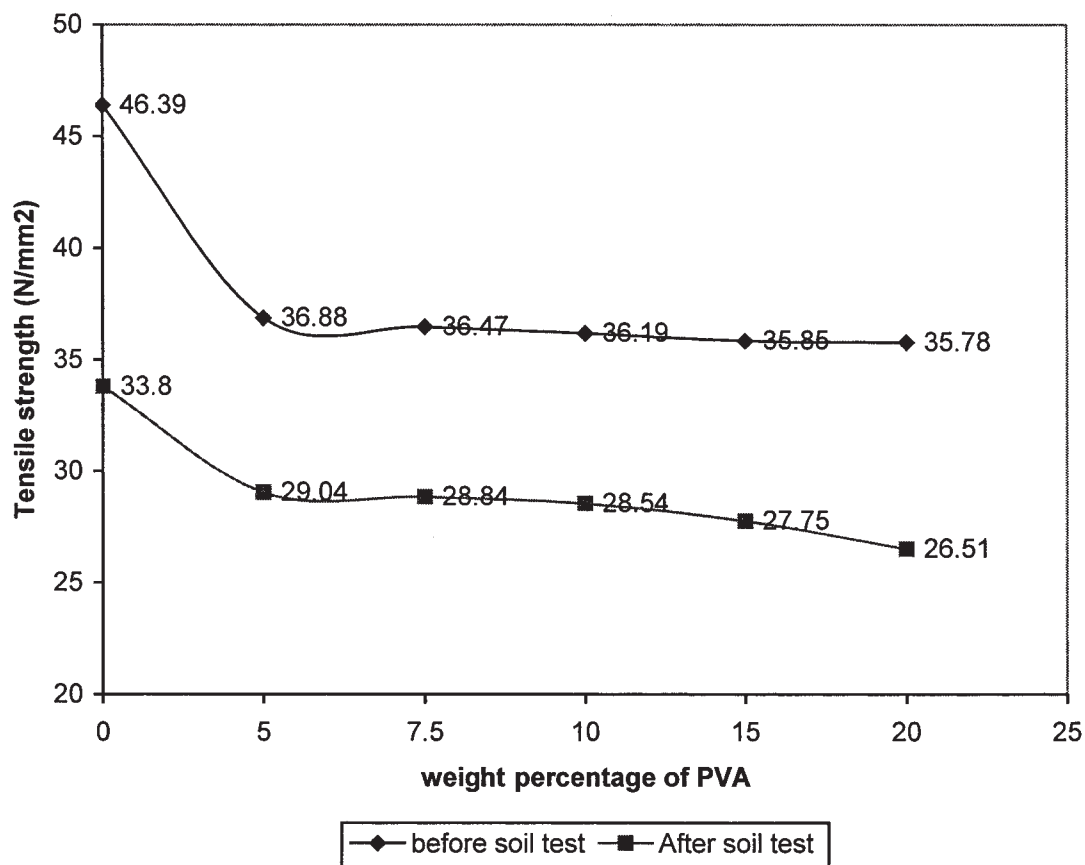


Figure 4 Effect of PVA on biodegradation of polyamide-6.

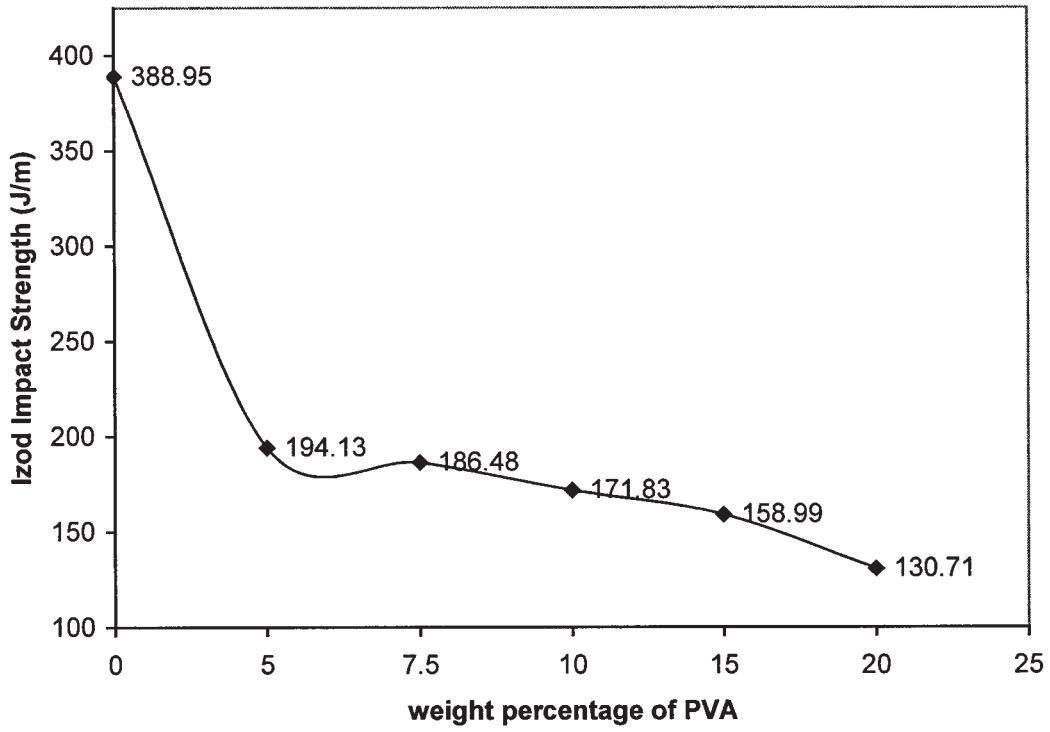


Figure 5 Effect of PVA addition on impact strength of polyamide-6.

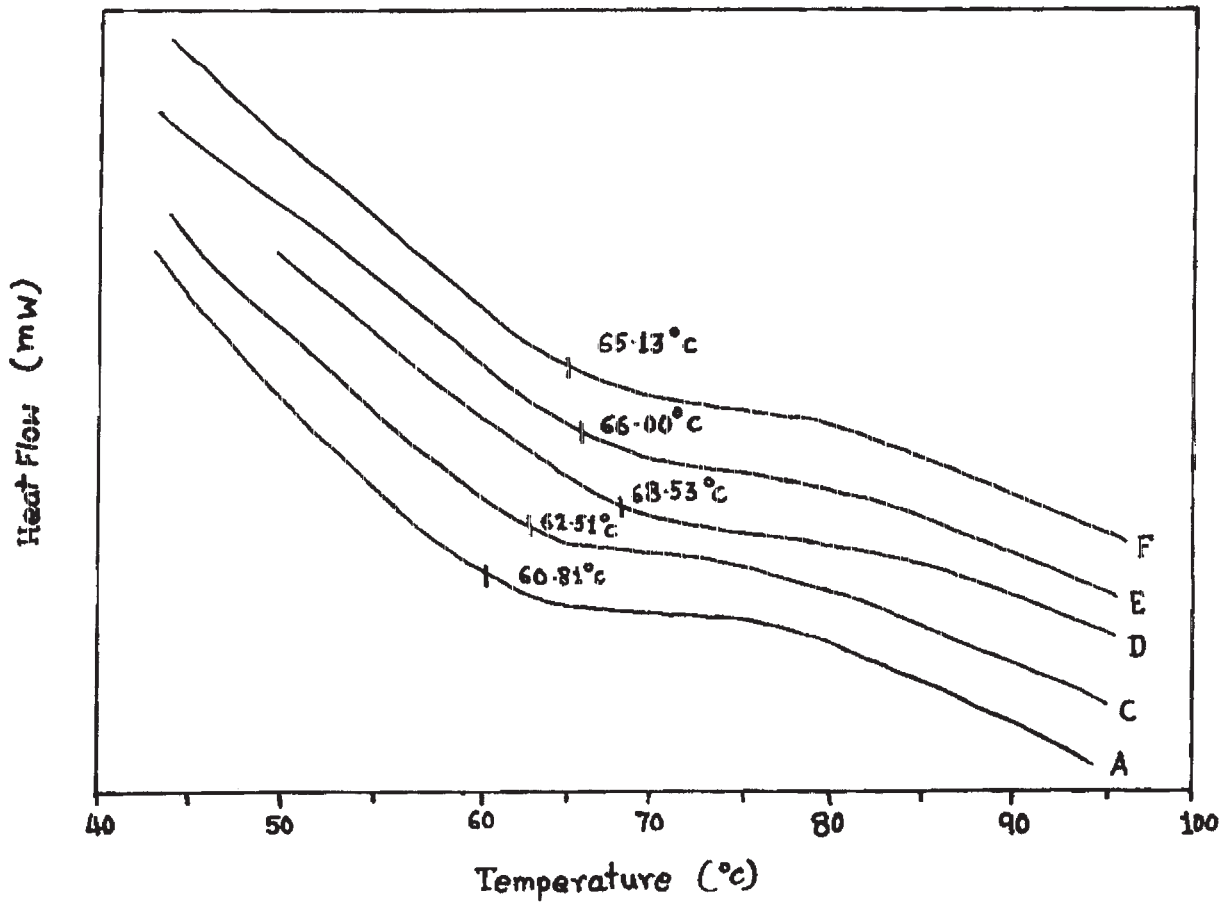


Figure 6 T_g of polyamide-6/PVA blends in DSC thermograms.

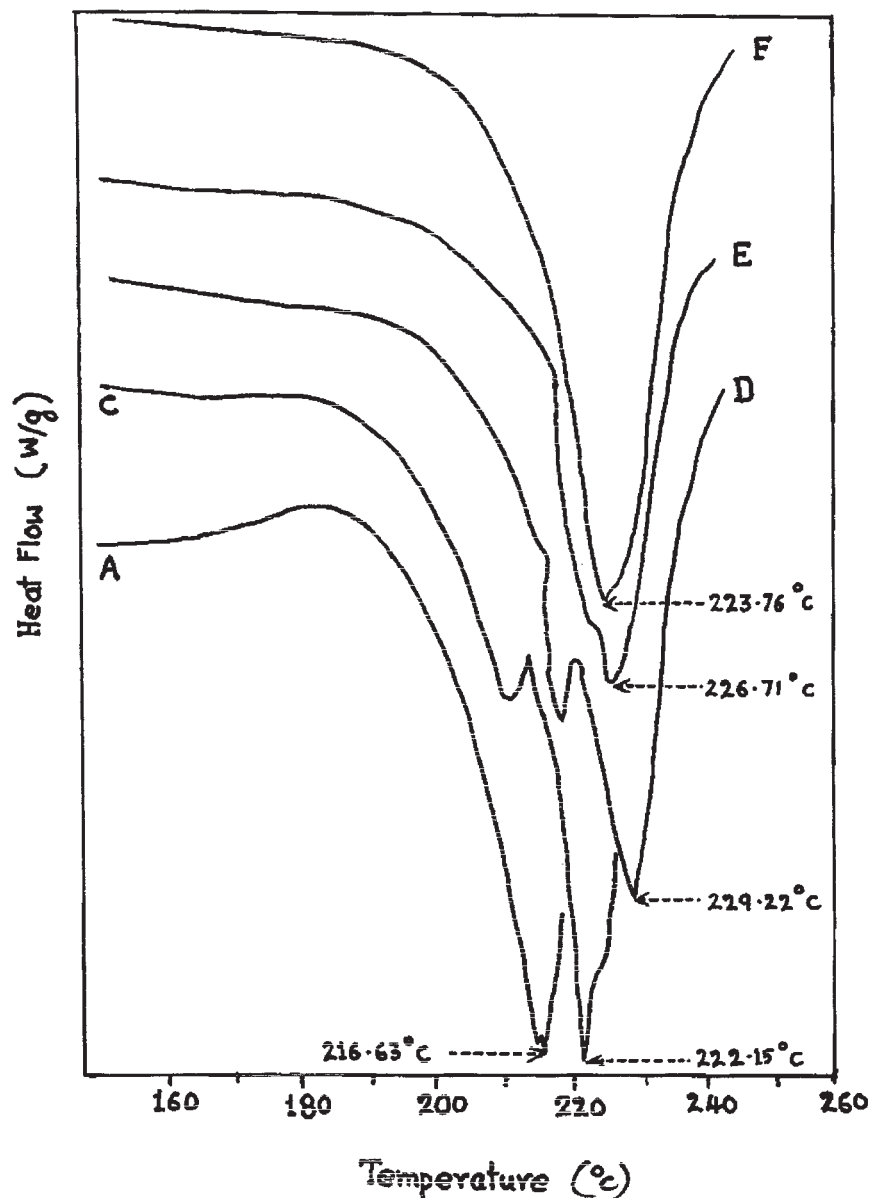


Figure 7 T_m of polyamide-6/PVA blends in DSC thermograms.

soil burial²⁸ provides qualitative indications of biodegradation. Generally, the samples are buried in soil for a period of up to 2 years, and at the end of the testing periods, changes in properties like weight, mechanical strength, shape, etc were studied. Most of the studies²⁹⁻³² on biodegradability have been based on the weight loss. However, some studies based on the strength loss have also been reported.^{33,34} In this investigation, tensile strength is measured for the tensile specimens made as per ASTM D 638 before and after soil burial test to evaluate the biodegradation (Fig. 4). The blend shows more loss in tensile strength and enhanced biodegradation than the virgin polyamide-6. This may be because PVA is most readily biodegradable polymer. The initial biodegradation

step involves the enzymatic oxidation of secondary alcohol groups in PVA to ketone groups, then hydrolysis of ketone groups results in chain cleavage.

Impact strength analysis

The impact strength of the polyamide-6 and PVA blends was shown in Figure 5. The impact strength decreased sharply in the initial stage, as in the case of tensile strength, but there after by increasing the PVA level, the impact values does not change appreciably from 7.5 to 20% PVA. In this case, the addition of PVA enhances the cohesive strength. When cohesive strength is more, the impact strength is less. So, with increase of PVA content, cohesive

TABLE II
Effect of PVA Addition on HDT and VSP
of Polyamide-6

S. No	Sample code	Heat deflection temperature (°C)	Vicat softening point (°C)
1	A	82.3	189.7
2	B	80.3	184.6
3	C	78.8	184.1
4	D	77.4	181.9
5	E	76.1	172.0
6	F	62.3	171.0

strength increases and impact strength decreases. This is due to the fact that introduction of PVA enhances intermolecular hydrogen bonding with increase of PVA content.

DSC analysis

Many techniques have been used to determine the miscibility of polymer blends. The most widely used criterion relies on the measurement of glass transition temperature (T_g) by DSC. The DSC thermograms of polyamide-6 and PVA were shown in Figures 6 and 7. From the thermograms, it can be observed that the T_g of virgin polyamide-6 is at 60.81°C and the blends showed substantial shift in T_g from 62.51 to 68.53°C as seen in Figure 6, which is higher than that of virgin polyamide-6. The detection of T_g' , whose value falls somewhere between T_g 's of the component polymer, is an indication of miscible system. The T_g value reported is the temperature at which the ordinate reaches midpoint between extrapolated baselines before and after the transition. This miscible system shows significant broadening of glass transition because the T_g 's of individual components are closer to each other. In this study, the elevation in T_g and T_m values of blends indicates the miscibility between two polymeric components. This tendency may be explained by intermolecular interactions between the amide groups of polyamide-6 and hydroxyl groups of PVA. The higher molecular attraction leads to higher melting point and T_g because of high cohesive energy density and their crystalline state. To a large extent, the factors, which determine the position of glass transition temperature, chain stiffness, and intermolecular force, also determine the melting point of a crystalline polymer.

Tests for elevated temperature performance

Many factors are considered when selecting a material for a high temperature application. In this regard, HDT and VSP are the two important factors. The HDT and VSP values of polyamide-6/PVA blends were shown in Table II, which indicates marginal decrease

TABLE III
Effect of PVA Addition on MFJ and Density of
Polyamide-6

S. No	Sample code	Melt flow index (g/10 min)	Density (g/cc)
1	A	7.466	1.126
2	B	8.348	1.1343
3	C	8.000	1.1405
4	D	7.730	1.1455
5	E	6.640	1.1473
6	F	6.000	1.1504

in HDT as well as VSP values with the incorporation of PVA. This may be due to the higher flexibility of PVA material.

Melt flow index and density

The results of MFI and density were presented in Table III. Considering the flow behavior, it was observed that MFI values of polyamide-6/PVA blends decreased when there is an increase in PVA content, because addition of PVA into the polyamide-6 matrix restricts the free mobility, which in turn increases the material density as shown in Table III. The reduction in MFI and enhancement in density indicate the qualitative interaction between polyamide-6 matrix and PVA domains.

Water absorption and hardness

PVA is a hydrophilic synthetic polymer. It can absorb water up to 10 times of its weight²³ on dry weight basis, when soaked in excess water at 25°C, whereas polyamide-6 absorbs water up to 1.336% only. Because the ratio of amide group with respect to the number of carbon atoms in polyamide-6 is less when compared with the ratio of hydroxyl groups with respect to the number of carbon atoms in PVA. So, with the addition of PVA, there is an increase in water absorption due to increase in hydroxyl groups. Table IV shows water absorption of all polyamide-6/PVA blends increased gradually. This may be due to increase in the freely

TABLE IV
Effect of Addition of PVA on Water Absorption and
Hardness of Polyamide-6

S. No	Sample code	Water absorption (%)	Hardness (shore A)
1	A	1.336	88.0
2	B	1.487	78.2
3	C	1.505	77.2
4	D	1.588	68.8
5	E	1.882	68.2
6	F	2.135	68.0

available hydroxyl groups, which will absorb water as expected. Interestingly, the overall increase in water absorption is not so high in proportion to the very high water absorption of PVA.²³ This may be because the PVA material was well covered by the continuous polyamide-6 matrix, and possibility of exposure to water was independent of PVA content.

CONCLUSIONS

Polyamide-6 blends were prepared with PVA at different compositions. The blends were subjected to biodegradation in soil. All the blends showed biodegradability in soil test in terms of reduction in tensile strength. From the above results, it is clear that the polyamide-6/PVA blends show enhanced biodegradation, water absorption, and density, but it is observed that the introduction of PVA into the polyamide matrix shows considerable reduction in tensile strength, impact strength, HDT, VSP, and hardness initially, but subsequent addition does not show significant reduction in these properties because of the interaction between amide groups of polyamide-6 and hydroxyl groups of PVA. The DSC results show miscibility between the two polymeric components.

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