

2

Polyethylene-g-Maleic Anhydride, a Compatibility Booster in Low Density Polyethylene and Polyvinylacetate Blend Preparations

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Low density polyethylene (LDPE) and polyvinyl acetate (PVAc) blends containing different weights percentages of PVAc, were prepared. Polyethylene graft Maleic anhydride (PE-g-MA) containing 0.4 mole% of anhydride groups was used as compatibility booster in the blends. FTIR helped confirming the blend formation. Improvement in mechanical properties as a result of blending and compatibilization have been observed. The properties of these blends were compared with those of blends of LDPE with NBR and SBR. Thermal properties were examined by the use of thermogravimetric analyser.

Keywords: Polyethylene-g-maleic anhydride; Low density PE; Polyvinylacetate; Polymer blends

INTRODUCTION

Emergence of plastics as a material has gone to the extent of surpassing steel in tons. It has found applications in place of paper, glass and metal [1]. Polymer modification through blending has received rapidly growing interest, during last several decades. Technical and economical considerations have given polymer blends a

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major share in the increasing sales of plastics [2, 3]. This applies both to the general purpose and to the higher value added material. Thus a significant number of commercial blends have become available and continuous efforts are expected to further create more desirable mechanical and thermal properties [4, 5].

Polyolefins cover almost 90% of the world plastic market. With excellent properties range polyolefins fail to provide biodegradation character. Thus, in the absence of knowledge to handle the plastic waste it has become an environmental threat. Efforts are to minimize these difficulties by blending LDPE with other polymer *viz.*, PVAc. Polysaccharides (cellulose, starch, amylose and their derivatives) are reported to have been blended with LDPE in order to impart biodegradability to the plastic [6–10]. But the hydrophilicity of natural polysaccharides comes as a constraint to incompatibility with LDPE and further it hampers the mechanical and electrical properties of the latter [11]. Blending of polyethylene with other synthetic polymer, rubbers and copolymer such as PP, polyester, polystyrene, polyamide, PET, PC, modified EPDM and BR, styrene-maleic anhydride copolymer have been reported [12–19].

Looking to the above said difficulties, PVAc goes as a suitable material to be blended with LDPE. To achieve a homogenous texture blending by solution method aided with a compatibilizer (LDPE-g-MA) has been used in the present work. Many compatibilizers have been used for improving the mechanical properties of LDPE blends *viz.* Ethylene acrylic acid (EAA), ethylene vinyl alcohol (EVOH), styrene maleic anhydride and ethylene propylene graft maleic anhydride has been reported earlier [20–24].

Nonsuitability of mechanical mixing of LDPE and PVAc followed by oxidative degradation possibilities at elevated temperature restricted us to prepare the blends by mechanical mixing and melt mixing process. Solubility of PE, PVAc and LDPE-g-MA in xylene tempted us to prepare the blends by solution mixing process as it decreases the possibility of noncompatibility and thermal degradation. Thus, blend prepared by above said method was cast in sheets and tested for mechanical, thermal and spectral properties. Improvement of mechanical properties is attributed to the reduction of interfacial tension at the interface of the components as well as penetration of surface molecules into the polymeric bulk [25].

EXPERIMENTAL

Materials

LDPE from Indian Petrochemical Ltd., Baroda, Gujarat, PVAc and Maleic Anhydride by National Chemical Baroda, solvents and other laboratory chemicals were used after routine purification, and they were of LR grade.

Grafting of Maleic Anhydride onto LDPE

A three necked flask equipped with reflux condenser, stirrer and nitrogen gas inlet was charged with LDPE and Maleic Anhydride and Xylene. Benzoyl peroxide was used as an initiator. The system was flushed out with inert gas to avoid any possibility of oxidation. Nitrogen gas flow was continued for the period of 4 hrs under the reflux condition at 120°C with constant stirring. Grafted product was poured into methanol, filtered and vacuum dried. Grafted product was used as a compatibility booster.

Blending and preparation of polymer sheet was performed as reported [26].

Analysis

1. Mechanical properties of the blend were measured in accordance with ASTM-procedures which are summarised in Table I.
2. Infrared spectral analysis were carried out in a Nicolet impact 400D FTIR spectrophotometer, made in USA. Samples were measured in the form of KBr pellets which were prepared by press molding.

TABLE I Properties and corresponding ASTM procedure of the blend

<i>Properties</i>	<i>ASTM procedure</i>
Melt flow index	D 1238-53T
Flexural strength	D 790
Tensile strength	D 638
Heat distortion temperature	D 648
Durometer hardness	D 2240-75

3. Thermal response of the samples was measured on DuPont Thermogravimetric analyser under nitrogen atmosphere at a heating rate of 20°C per minute and the percent weight loss as a function of temperature was scanned upto 950°C. IPDT were calculated following equation [27].

$$\text{IPDT} = (T_2 - T_1) \times A/A^* + T_1$$

RESULTS AND DISCUSSIONS

Melt Flow Index (MFI)

Melt flow is a measure of amount of material which flows through the orifice at 190°C under a load of 2.16 kg during a period of 10 minutes. High values of MFI indicates a better flow at an elevated processing temperature leading to a perfect molding and ease of processing at relatively low temperature. MFI results are tabulated in Table II.

All the MFI values for the blends were greater than LDPE. Addition of Graft copolymer (LDPE-g-MA) as compatibilizer increased the flow. This indicates the lower melt viscosity of the blend which is advantageous from processing point of view. This shows the effectiveness of compatibilizer as a processing aid.

Flexural Strength

A three point loading system utilizing central loading in a single supported beam was used for measurement. A cross head speed of

TABLE II Melt flow index (MFI)

Ratio	MFI gm\$/10 min	
	Non compatibilized	Compatibilized
LDPE: PVAc		
1:0	0.5	0.5
1:0.25	0.91	1.02
1:0.5	1.3	1.53
1:0.75	1.67	2.77
1:1	2.01	4.78
0.75:1	4.26	7.12
0.5:1	5.08	8.57
0.25:1	6.67	9.85

2.5 cm/min was used for all specimens. Results are tabulated in Table III.

All flexural strength values for these blends were greater than LDPE. Flexural strength of blends with and without compatibiliser were almost the same.

Tensile Strength

Measurement of mechanical properties such as elongation at break and tensile properties were performed on tensile tester at room temperature. A crosshead speed of 10 cm/min were used in all measurements. Three measurements were conducted for each sample and the results were averaged to obtain a mean value. Tensile strength and % elongation of both the blends are tabulated in Table IV.

The higher values of tensile strength and percent elongation were obtained due to addition of PVAc in the blends prepared with and without compatibilizer upto 1:1 LDPE:PVAc composition. The

TABLE III Flexural strength

Ratio <i>LDPE:PVAc</i>	Flexural strength kg/cm^2	
	<i>Non compatibilized</i>	<i>Compatibilized</i>
1:0	69.63	69.63
1:0.25	70.25	70.00
1:0.5	73.87	73.25
1:0.75	78.50	77.10
1:1	86.92	84.53
0.75:1	97.17	93.29
0.5:1	112.82	101.72
0.25:1	197.43	183.15

TABLE IV Per cent elongation and tensile strength

Ratio <i>LDPE:PVAc</i>	% elongation % (Mean)		Tensile strength kg/cm^2 (Mean)	
	<i>Non</i>		<i>Non</i>	
	<i>compatibilized</i>	<i>Compatibilized</i>	<i>compatibilized</i>	<i>Compatibilized</i>
1:0	100	100	31	31
1:0.25	133	133	35	37
1:0.5	166	166	38	41
1:0.75	200	225	40	45
1:1	266	295	55	58
0.75:1	300	336	54	60
0.5:1	333	389	50	61
0.25:1	400	450	47	63

increased amount of PVAc in non-compatibilised blend gave lower valued of tensile strength but higher values of % elongation. The high values of both properties were observed in case of compatibilised blend.

Heat Distortion Temperature (HDT)

Heat distortion under load data are tabulated in Table V. It is clear that HDT increases with increasing the amount of PVAc for compatibilized and noncompatibilized blends. HDT of LDPE was observed 42°C and it increases up to 70°C and 81°C for noncompatibilised and compatibilised blends respectively.

Durometer Hardness (DH)

Durometer hardness measurements represent the hardness of material when it is subjected to a certain force through a penetrating object of well defined dimensions. DH is measured in terms of shore A and shore D. DH was measured for both types of blends and the obtained data are tabulated in Table VI. All the hardness values of the blends were lower than that of LDPE. Addition of graft copolymer increased the hardness but it was somewhat lower than that of LDPE.

Comparison

The data clearly indicate that the values of tensile strength, elongation at break, MFI, HDT, and Shore Hardness were higher in case of

TABLE V Heat distortion temperature (HDT)

Ratio <i>LDPE: PVAc</i>	HDT°C	
	<i>Non compatibilized</i>	<i>Compatibilized</i>
1:0	42	42
1:0.25	47	47
1:0.5	50	52
1:0.75	52	53
1:1	55	56
0.75:1	58	60
0.5:1	67	72
0.25:1	70	81

TABLE VI Durometer hardness

Ratio <i>LDPE: PVAc</i>	<i>Durometer hardness</i>			
	<i>Shore A</i>		<i>Shore D</i>	
	<i>Non compatibilized</i>	<i>Compatibilized</i>	<i>Non compatibilized</i>	<i>Compatibilized</i>
1:0	90	90	40	40
1:0.25	88	88	38	38
1:0.5	87	87	35	37
1:0.75	85	86	33	36
1:1	84	84	29	33
0.75:1	75	79	27	30
0.5:1	72	77	23	28
0.25:1	68	75	21	25

TABLE VII Comparison of blends with rubber - LDPE blends

<i>Type of blend</i>	<i>LDPE content</i>	<i>Tensile strength</i>	<i>Per cent elongation</i>
LDPE: PVAc (Non compatibilized)	25	47	400
	50	55	266
	75	54	300
LDPE: PVAc (Compatibilized)	25	63	450
	50	58	295
	75	60	336
NBR: LDPE	25	21	355
	50	32	340
	75	35	230
SBR: LDPE	25	18	200
	50	29	160
	75	34	180

addition of compatibiliser. The values obtained in case of blends without compatibiliser were lower. The general trend observed was not same for the flexural strength. It was lower in case of blends synthesised with compatibiliser. The properties of blends synthesised are compared with that of LDPE-rubber blends. The comparison is summarised in Table VII. From the comparison it was concluded that both the types of blends have better mechanical properties than those of LDPE-NBR and LDPE-SBR blends.

Infrared Spectroscopy

The spectral analysis of noncompatibilised and compatibilised blend and LDPE-g-MA were carried out by means of IR spectroscopy.

From the perusal of Figures 1, 2(a) and 2(b), IR spectra show sharp peak around 1752 cm^{-1} confirming the presence of ester linkages in PVAc in a blend. A sharp absorption band at 1031 cm^{-1} is attributed to the aliphatic olefins— $(\text{CH}=\text{CH})_n$ present in the blend based on LDPE. C—O stretching band is observed at 1254 cm^{-1} . Sharp band around 2925 cm^{-1} determines the vibration stretching of $-(\text{C}-\text{H})-$ and $-(\text{CH}_2)-$ present in LDPE. Peaks due to carbonyl stretching vibration of anhydride group at 1717 cm^{-1} and 1730 cm^{-1} in Figure 2(a) were observed. The presence of above key peaks in IR spectra supports but not confirms the synthesis of LDPE:PVAc blend, LDPE-g-MA and compatibilised blend of LDPE:PVAc.

Thermogravimetric Analysis

The blend of LDPE with PVAc showed two decomposition stages as presented in Figure 3. The first decomposition occurs at 285°C to 425°C which is attributed to PVAc decomposition, the structure of PVAc is branched, brownian movement within the molecules occurs more rapidly compared to straight chain LDPE polymer. The second

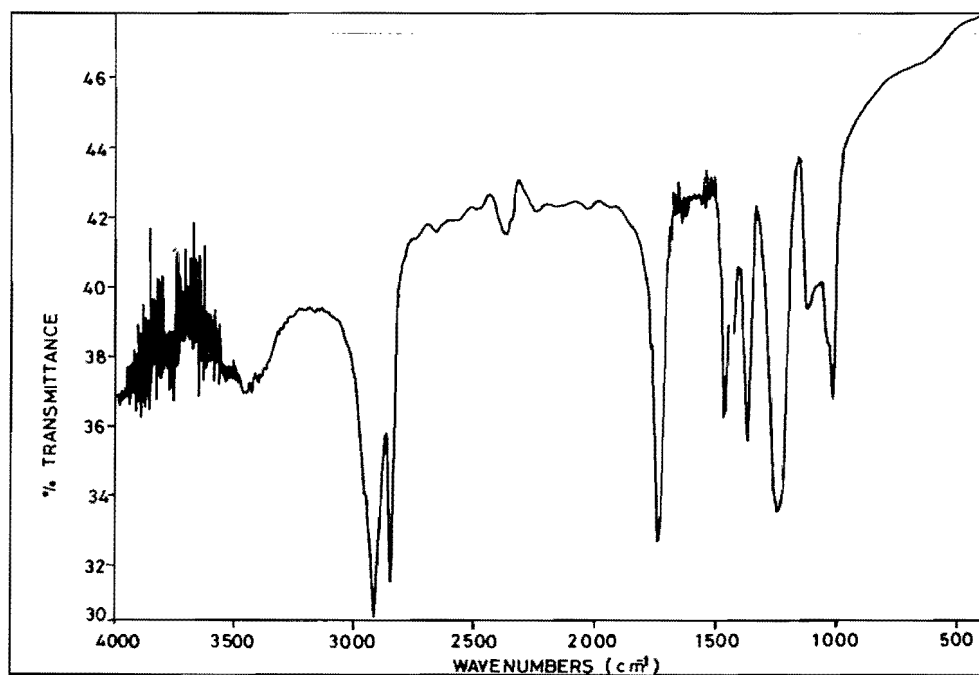


FIGURE 1 Blends of LDPE and PVAc.

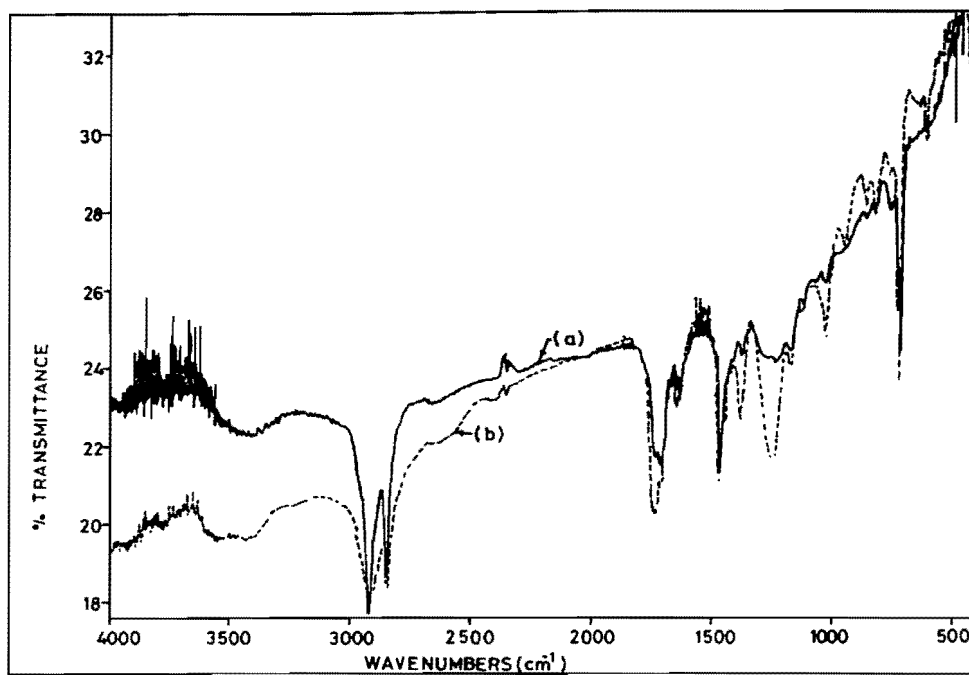


FIGURE 2 (a) LDPE graft maleic anhydride; (b) Blend of LDPE graft maleic anhydride and PVAc with LDPE.

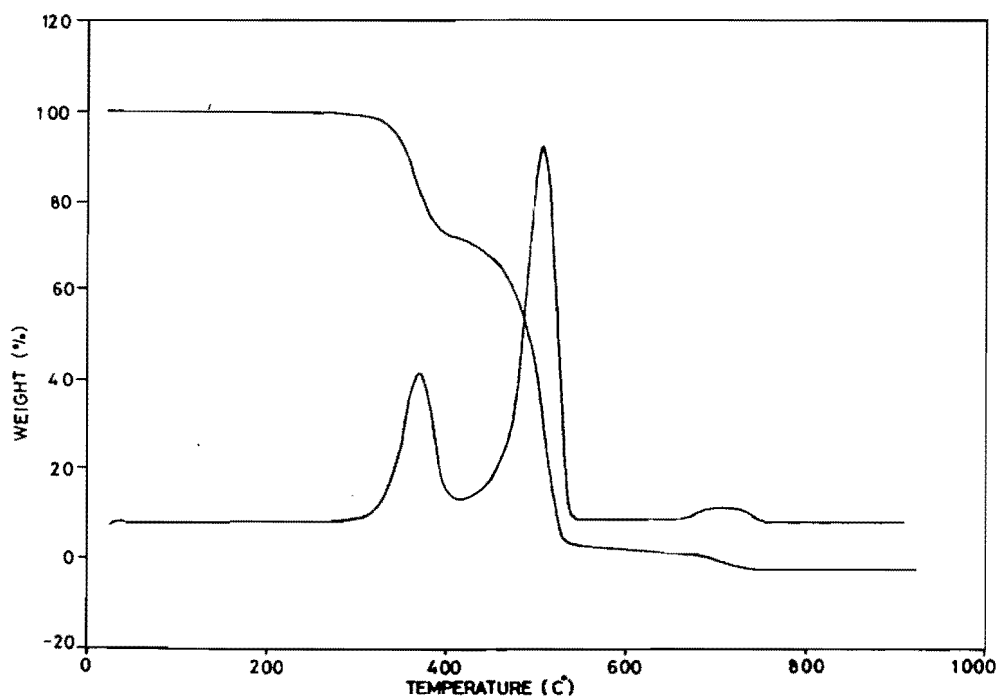


FIGURE 3 TGA curve of LDPE and PVAc blend.

stage, appearing at higher temperature at about 510°C was due to LDPE decomposition. There was no weight loss observed upto 275°C. IPDT of the blend was found at 534°C. Thus, blend offers a wide range of processing temperature.

CONCLUSION

From this study we observed the strong effect of addition of compatibiliser. The enhanced values of tensile strength, elongation at break, MFI, HDT, and durometer hardness were observed at 10% by weight compatibiliser. The lower values of the properties obtained for the blends of LDPE-PVAc synthesised without compatibiliser clearly indicate the effect of addition of compatibiliser. In all the blends synthesised 10% weight compatibiliser was used.

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