

## CHEMICAL MODIFICATION OF BLENDS OF POLY(VINYL CHLORIDE) WITH LINEAR LOW DENSITY POLYETHYLENE

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**Abstract**—The effects of modifying blends of poly(vinyl chloride) (PVC) with linear low density polyethylene (LLDPE) by means of acrylic acid, maleic anhydride, phenolic resins and *p*-phenylene diamine were investigated. Modification by acrylic acid and maleic anhydride in the presence of dicumyl peroxide was found to be the most useful procedure for improving the mechanical behaviour and adhesion properties of the blend. The improvement was found to be due mainly to the grafting of the carboxylic acid to the polymer chains; grafting was found to be more effective in LLDPE/PVC blends than in pure LLDPE.

### INTRODUCTION

Recycling by reprocessing of plastic waste presents a solution to the major problem created by the plastic consumer society. This method of re-utilization of solid plastic waste is used for producing secondary products, so lowering energy costs and reducing environmental pollution. Polyethylene (PE) is a major component of plastic waste. 80% of PE waste is contaminated with other polymers, mainly poly(vinyl chloride) (PVC) [1, 2]. Separating these polymers and then recycling them individually introduces an additional costly step in the reprocessing. Reprocessing of mixed plastic waste is becoming more popular in view of the economic benefits. The PVC/PE blend is now utilized in several applications e.g. blister packaging, electric cable sheathing [3, 4] but the physico-mechanical properties and the technical performance of the PVC/PE blend are much inferior than those of PVC or PE individually mainly because of the thermodynamic incompatibility. Various methods have been suggested for the reactive compatibilization of the immiscible blends for demanding applications [5, 6]. Moderate improvement in the physical and mechanical properties is achieved by the incorporation of polymeric modifiers (such as CPE, EPDM and SBS) in PVC/PE blends [7-9]. The deterioration in mechanical properties is also reduced by co-crosslinking the PVC/PE blend using dicumyl peroxide [8]. Functionalization or chemical modification of the polymers is another common means for improving the physical and mechanical properties of the blends [10-12].

This paper reports the functionalization of PVC/LLDPE (linear low density polyethylene) blend as a possible means for improving its mechanical behaviour. Acrylic acid, maleic anhydride, phenolic resin and *p*-phenylene diamine were used for the chemical modification. The effects of such modification on the adhesive bond strength of the blends with metallic surfaces have been also investigated.

### EXPERIMENTAL PROCEDURES

#### Materials

PVC: powder; suspension polymer; K value = 67 (Supplied by IPCL, Baroda).

LLDPE: ladene 218 W; Melt index (g/10 min) = 2.0. Density (g/cm<sup>3</sup>) = 0.918. (Supplied by IPCL, Baroda).

Acrylic acid: LR Grade.

Maleic anhydride: LR Grade.

Phenolic resin 1: containing 9% hexamine; powder.

Phenolic resin 2: high methylol content (11%); light yellow clear lumps.

*p*-Phenylene diamine: LR Grade.

Di-cumyl peroxide: Aggregate state: crystal. purity = 99%. Density = 1.02. Recommended processing temperature = 160-200°C.

LLDPE/PVC blends of various compositions (PVC content from 0 to 50% of total polymer weight) were prepared on a Brabender Plasticorder Model PL3S equipped with roller mixing heads. The levels of modifiers and stabilizers used for a 80/20 LLDPE/PVC blend are shown in Table 1 as an example.

#### Functionalization

(a) *Acrylic acid/maleic anhydride*. PVC with heat stabilizer (2.5 phr tribasic lead sulphate, TBLs) was melt-mixed with LLDPE at 150°C and 30 rpm. After 2 min, DCP (0.2 phr) was added as the free radical precursor, and then acrylic acid or maleic anhydride (3 phr) was added. Mixing was continued for another 3 min.

(b) *Phenolic resin modification*. Mixing was done at 180°C and 30 rpm. After melt-mixing of PVC and LLDPE, phenolic resin was added, with SnCl<sub>4</sub> as accelerator. After 3 min, MgO was added to neutralize the free acid. The total mixing time was 8 min.

(c) *p*-Phenylene diamine modification. The mixing conditions were 180°C and 30 rpm. *p*-Phenylene diamine (3 phr) was added after the melt-mixing of PVC and LLDPE. The mixing was continued until the torque reached a steady value.

Test samples were prepared by compression moulding at 180°C for 3 min in a laboratory hydraulic press. Tensile properties were determined according to ASTM D 638 on a Zwick universal testing machine model 1445 using a crosshead speed of 50 mm/min.

Table 1. Recipe for the blend with 20% PVC

<b>I. PVC and stabilizer</b>	
PVC	—8 g (20% of total polymer)
TBLS	—0.2 g (2.5 phr of PVC)
<b>II. PE-LLD</b>	
LLDPE	—32 g
<b>IIIa. Modifier I</b>	
Acrylic acid	—1.2 g (3 phr of total weight)
DCP	—0.08 g (0.2 phr of total weight)
<b>IIIb. Modifier II</b>	
Maleic anhydride	—1.2 g (3 phr of total weight)
DCP	—0.08 g (0.2 phr of total weight)
<b>IIIc. Modifier III</b>	
<i>p</i> -Phenylene diamine	—1.2 g (3 phr)
<b>IIId. Modifier IV</b>	
Phenolic resin	—1.2 g (3 phr) (having high methylol).
SnCl <sub>2</sub>	—0.16 g (0.4 phr of total weight)
MgO	—0.003 g (0.07 phr of total weight)
<b>IIIe. Modifier V</b>	
Phenolic resin	—2: 1.2 g (containing hexamine)
SnCl <sub>2</sub>	—0.16 g (0.4 phr)
MgO	—0.003 g (0.07 phr).

Infrared spectra of the modified blends (excess carboxylic acid free) were taken with a Beckman i.r. spectrophotometer. The adhesive bond strengths between metal and the modified polymer blends were assessed from the resistance to peeling of a 25 mm strip polymer sample from the metal surface, angle of peeling being 180°, at 50 mm/min test speed. The chemical resistance of a modified blend was determined by keeping it in contact with reagents at ambient temperatures for one week and then noting the percentage change in weight as per ASTM 471 (1983). The dimensional stabilities of modified blends in hot water and hot oil were determined by keeping the samples at 70°C for 24 hr.

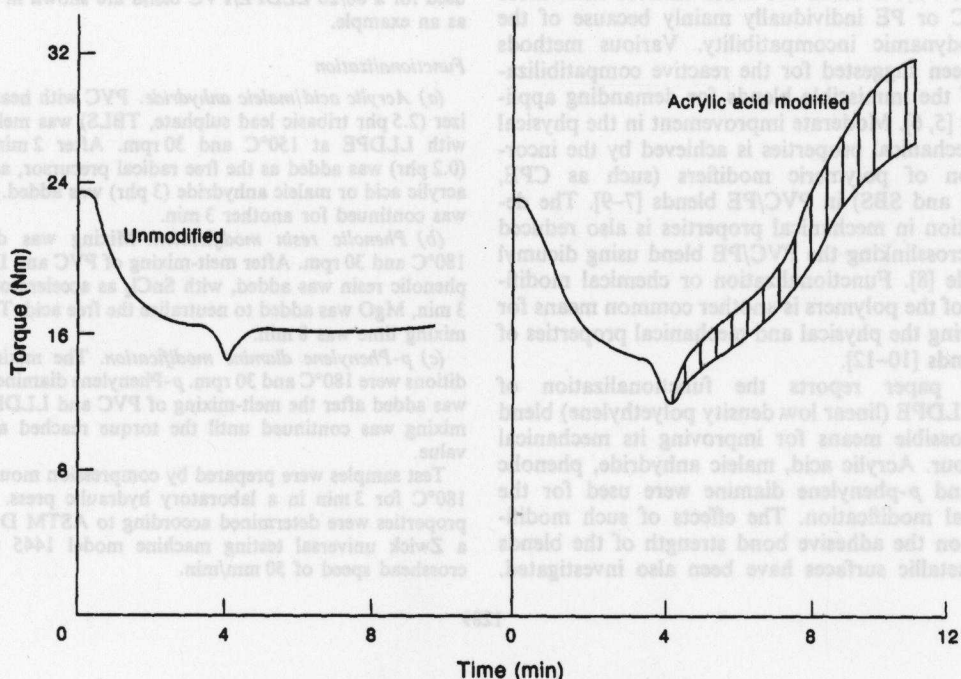


Fig. 1. Brabender torque curves of the 40/60 PVC/LLDPE blend.

## RESULTS AND DISCUSSION

Figure 1 shows the Brabender torque curves of the unmodified and acrylic acid modified PVC/LLDPE (40/60) blends at 180°C. A large increase in torque occurs with the addition of acrylic acid along with DCP (0.2 phr). The increase in torque (viscosity) is probably due to (i) co-crosslinking of the polymers in the presence of carboxylic acid and DCP and/or (ii) grafting of carboxylic acid to the polymer chains. Since the DCP concentration was low, the grafting of carboxylic acid is probably the dominating reaction [13].

The mixing temperature was found to be very critical for successful chemical modifications. When the mixer temperature was <180°C, the torque curves of the acrylic acid modified blends resembled the unmodified blends without any significant increase in torque values. Hence for preparing test pieces of the modified blends, mixing was done at 150°C and then compression moulding at 180°C for sufficient time for the modifying action to occur.

The preferred site for the grafting is possibly the tertiary carbon atom of LLDPE and the carbon atom to which the chlorine atom is attached in PVC. Grafting can give rise to strong interaction between the phases. Another observation is that, with increase of PVC content, there is a pronounced increase in the bandwidth of the torque curve at the end of mixing (Fig. 2). Similar behaviour was also observed when LLDPE alone was crosslinked with various concentrations of DCP. Hence it may be concluded that the increase in the bandwidth of the torque curve is due to higher crosslink density and that PVC is more susceptible to crosslinking and modification than LLDPE.

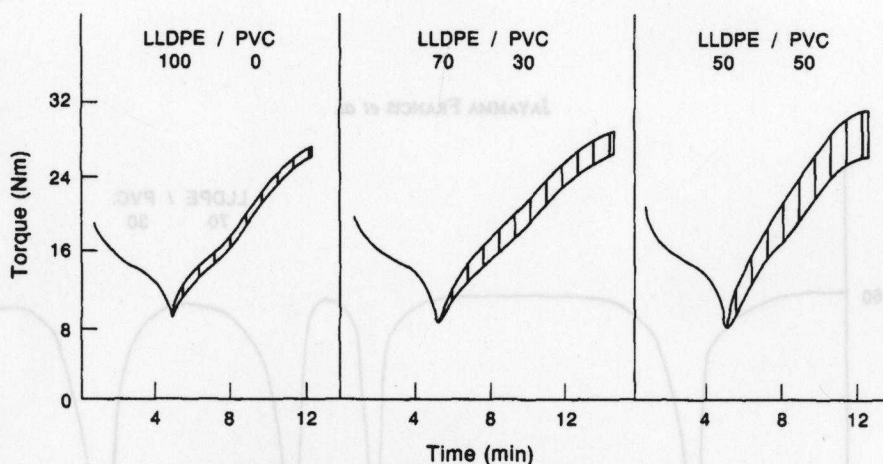


Fig. 2. Variation in the nature of Brabender torque with PVC content.

Figure 3 shows the i.r. spectra of unmodified, acrylic acid modified and acrylic acid-DCP modified LLDPE. It shows that acrylic acid grafting occurs only in the presence of DCP. The band at  $1730\text{ cm}^{-1}$  shows the presence of  $\text{C}=\text{O}$  groups. The i.r. spectrum of 30/70 PVC/LLDPE blend also shows acrylic acid grafting (Fig. 4).

The variation of tensile strength with composition for the unmodified and carboxylic acid modified PVC/LLDPE blends is shown in Fig. 5. Good improvement in tensile strength and yield stress is

found to follow the chemical modification. It is also found that increasing the concentrations of acrylic acid/maleic anhydride or DCP does not result in further improvement in properties. Figure 6 gives the effect of chemical modifications using phenolic resins and *p*-phenylene diamine on the tensile strength of PVC/LLDPE blends. The ability of phenolic resin to improve the ultimate properties of PE or PP blend with NBR has previously been reported [9]. Both types of phenolic resins (high methylol type and resin (containing hexamine) were used for

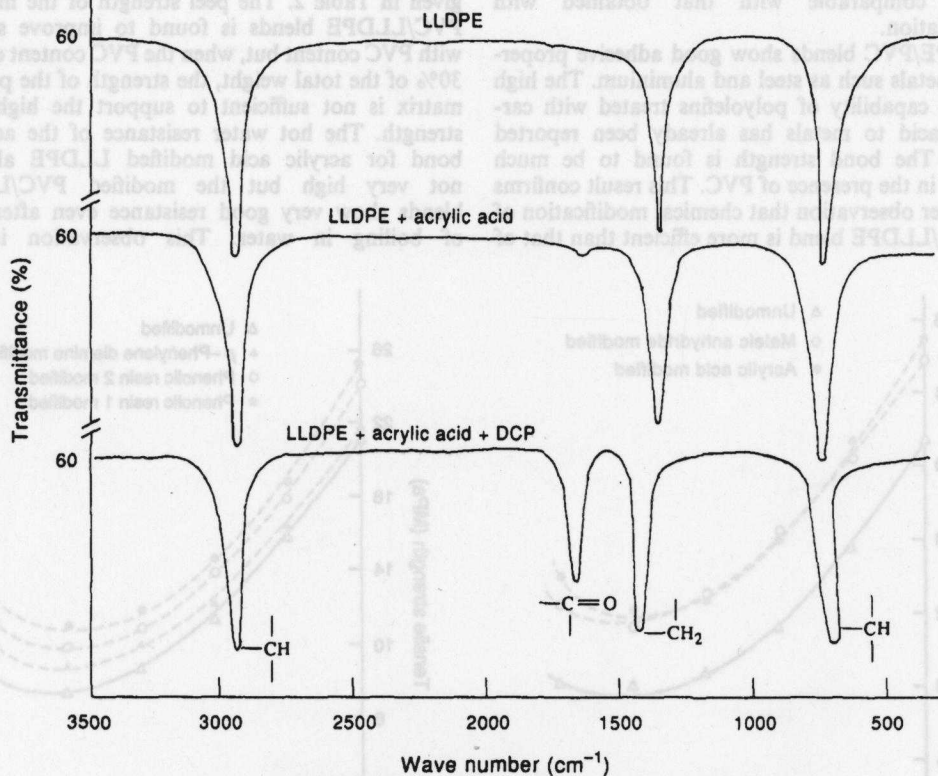


Fig. 3. Infrared spectra of unmodified and modified LLDPE.

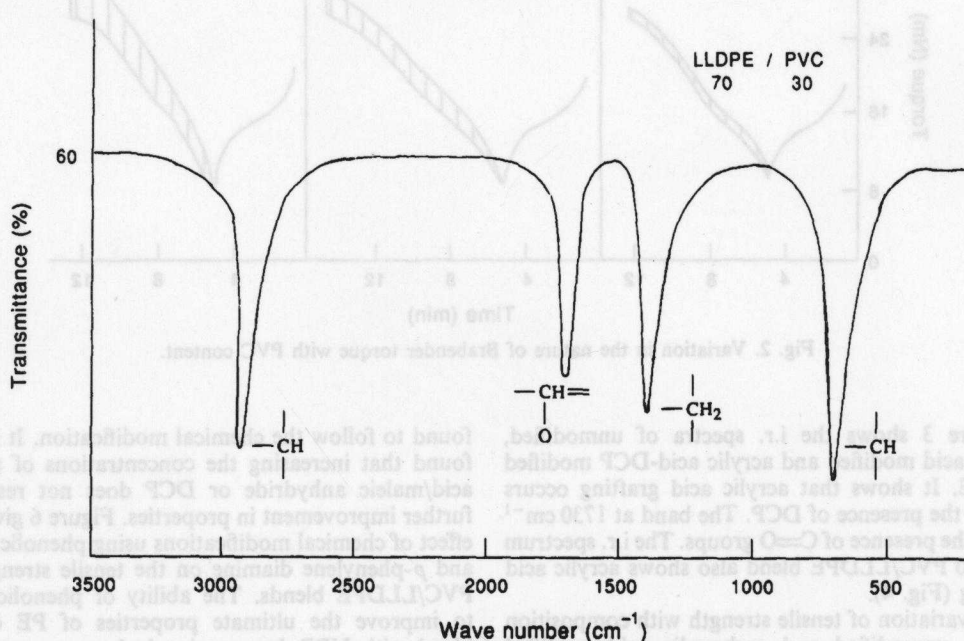


Fig. 4. Infrared spectrum of acrylic acid-DCP modified 30/70 PVC/LLDPE blend.

technological compatibilization. Even though these modifications result in marginal improvement, it is not comparable with that obtained with carboxylation.

LLDPE/PVC blends show good adhesive properties to metals such as steel and aluminium. The high adhesive capability of polyolefins treated with carboxylic acid to metals has already been reported [13, 14]. The bond strength is found to be much superior in the presence of PVC. This result confirms our earlier observation that chemical modification of the PVC/LLDPE blend is more efficient than that of

LLDPE alone. The peel strengths of the carboxylic acid modified LLDPE and its blend with PVC are given in Table 2. The peel strength of the modified PVC/LLDPE blends is found to improve steadily with PVC content but, when the PVC content exceeds 30% of the total weight, the strength of the polymer matrix is not sufficient to support the high bond strength. The hot water resistance of the adhesive bond for acrylic acid modified LLDPE alone is not very high but the modified PVC/LLDPE blends show very good resistance even after 50 hr of boiling in water. This observation is also

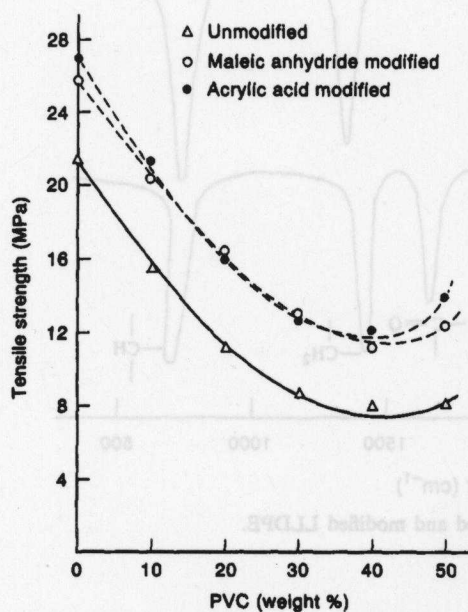


Fig. 5. Variation of tensile strength with composition of PVC/LLDPE blends.

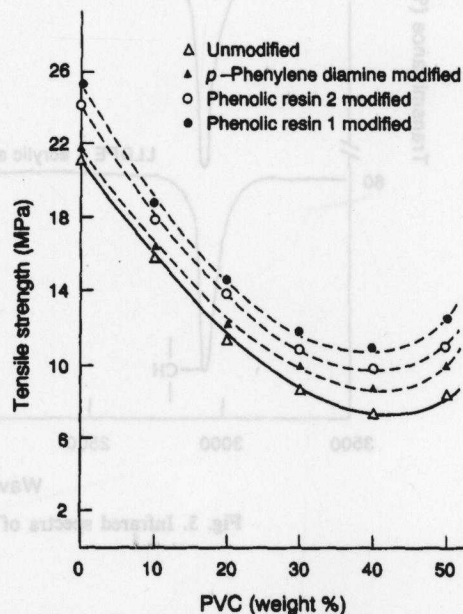


Fig. 6. Variation of tensile strength with composition of PVC/LLDPE blends.

Table 2. Peel resistance of carboxylic acid modified blends

Blend composition	Peel resistance (N/mm)			
	Acrylic acid treated		Maleic anhydride treated	
	Steel	Aluminium	Steel	Aluminium
LLDPE:PVC				
100 0	8.90	6.62	5.24	3.48
80 20	9.82	8.25	5.86	4.47
70 30	15.3	10.8	6.26	4.71
60 40	12.0	10.1	5.50	4.41
50 50	11.68	7.37	3.5	2.8

Table 3. Chemical resistance of acrylic acid modified blends

Blend composition	Percentage increase in weight				
	At room temperature for 7 days			At 70°C for 24 hr	
	Oil	Toluene	Conc.HNO <sub>3</sub>	Oil	H <sub>2</sub> O
LLDPE:PVC					
100 0	5.0	21.4	3.3	30.6	1.4
80 20	2.7	28.6	2.6	30.0	1.6
70 30	2.4	25.6	2.4	17.1	2.1
60 40	1.0	23.8	3.2	14.3	1.6
50 50	1.3	25.0	3.8	13.1	2.1

in conformity with the earlier observation that the presence of PVC increases the adhesive bonding strength.

The percentage increase in weight of the acrylic acid modified blends in oil, toluene and conc. HNO<sub>3</sub> are given in Table 3. The blends are found to have good resistance in these media. The blends also possess good dimensional stability in hot oil and hot water.

#### CONCLUSIONS

1. Functionalization of LLDPE/PVC blends using acrylic acid in the presence of DCP is a good

means for improving the mechanical behaviour of the blends.

2. Functionalized LLDPE/PVC blends show very good bond strength with metals such as steel and aluminium.

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