



## Utilization of Pulverized Cross-linked Polyethylene Foam as Effective Filler for Linear Low-Density Polyethylene

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Received 30<sup>th</sup> February 2014; Revised 22<sup>nd</sup> March 2014; Accepted 30<sup>th</sup> March 2014

### ABSTRACT

Cross-linked polyethylene foam (XPEF) is widely used in packaging and insulation applications. Since cross-linked polymer cannot be reprocessed similar to thermoplastics, utilization of these thermoset materials is an environmentally challenging problem. Due to thermoset nature, it can be used as filler or reinforcement in other base materials. Since cross-linked polyethylene will have a better compatibility with polyolefin matrix, using waste cross-linked polyethylene as filler in polyolefin material will be an attractive solution. First, XPEF was crushed to particles with mesh size of about seven and was used as filler in linear low density polyethylene (LLDPE) having 6.5 melt flow index. Concentration of waste cross-linked foam powder was varied up to 40 phr in LLDPE matrix. Tensile, flexural, impact, vicat softening temperature, heat distortion temperature, scanning electron microscopy, and rheological properties were analyzed for the prepared compositions. Impact strength of LLDPE is found to have increased by 380% on 40 phr addition of the foam powder in LLDPE matrix. Overall changes in mechanical properties are similar to cross-linked polyethylene. From scanning electron microscope images, it became evident that the waste cross-linked foam powder acted as a point of entanglement with different chains of LLDPE, giving physical cross-linking.

**Key words:** Foam, Cross-linking, Polyethylene, Filler.

### 1. INTRODUCTION

Cross-linked polyethylene foams (XPEFs) are commercially available insoluble and infusible polymers formed by the cross-linking reactions between the polymer chains with the help of several functional groups; which converts these thermoplastic materials into thermosets [1]. Several types of these cross-linking reactions are described in detail by Narkis and Miltz [2]. These XPEFs are produced either by the process of extrusion, injection molding, or compression molding. They find wide applications in rotomolded products, packaging and electrical insulations [2,3].

However, these foam materials are nonbiodegradable and non-re-processable due to the cross-linking formed in their structure [4]. Thus, if disposed off, they can pose an environmental threat due to their nonbiodegradability and health hazard to animals if consumed unknowingly. Therefore, it is very much essential to find a proper way to dispose of these materials. Land filling is a traditional option utilized in

developing countries like India, China, Sri Lanka etc., but cannot prove useful in the long run mostly due to the increasing cost of the land [5]. Recently, Tamboli et al. suggested an economical and environmental friendly way to get rid of these materials, by utilizing it as filler in thermoplastic materials like high-density polyethylene (HDPE) [6]. They reported a six-fold improvement in the impact property of HDPE by incorporation of about 40 phr of the crushed XPEF in it. However, no study is reported regarding the utilization of this waste, environmentally hazardous material as filler in other commercially available polyolefins.

Accordingly, in the present research work, an attempt is made to utilize this waste crushed XPEF particles as filler in linear low-density polyethylene (LLDPE). Concentration of the crushed XPEF was varied as 10, 20, 30, and 40 phr in LLDPE and the prepared compositions were characterized for mechanical, vicat softening temperature (VST), heat distortion temperature (HDT), rheological and morphological properties.

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## 2. EXPERIMENTAL

### 2.1. Materials

LLDPE, commercial name: E24065, density: 0.924 g/cc, melt flow index (MFI): 6.5 g/10 min at 190°C using a 2.16 kg load was obtained from Reliance Industries Pvt. Ltd., Mumbai, India. Waste XPEF prepared from a mixture of linear low-density polyethylene and low-density polyethylene, having gel content of 75-80%, was procured from Supreme Industries Pvt. Ltd., Mumbai, India. The foam was pulverized XPEF (PXPEF) into a fine powder of mesh size 7 and was found to have a density of about 800 kg/m<sup>3</sup>. Finalux G3 (wetting agent) was supplied by Fine Organics Pvt. Ltd., Mumbai, India.

### 2.2. Preparation of LLDPE/PXPEF Compositions

#### 2.2.1. Dry blending

LLDPE and PXPEF were dried in an air-circulating oven at 80°C for 5 h to remove any adsorbed and absorbed moisture. Dry blending of LLDPE and PXPEF was performed in a tumbler mixer for 5 min using Finalux G3 (0.2% w/w of LLDPE+PXPEF) as the wetting agent.

#### 2.2.2. Melt blending

LLDPE/PXPEF compositions at 10, 20, 30, and 40 phr of PXPEF loadings were prepared by melt compounding using a laboratory co-rotating, intermeshing twin-screw extruder (Model: MP 19 PC, APV Baker, UK) with L/D = 20 equipped with a circular die of 2 mm diameter. A screw speed of 80 rpm was used, and the temperature profile of 160, 175, 210, 220, and 230°C from the hopper to the die was maintained constant. Extruded strands were water cooled (30°C) and pelletized.

#### 2.2.3. Injection molding

Pellets, obtained from the extrusion operation, were dried in an air-circulating oven at 80°C for 5 h. Injection molding (Boolani Machineries India Ltd., Mumbai, India) was performed by maintaining the temperature profile as 190, 210, and 230°C from the hopper to the ejection nozzle. Standard ASTM samples for tensile (ASTM D638), flexural (ASTM D790), and impact (ASTM D256) testing were obtained from injection molding. The formulations prepared and their nomenclature are as shown in the Table 1.

## 3. CHARACTERIZATION AND TESTING

### 3.1. Mechanical Properties

Tensile (tensile strength and percentage elongation at break) and flexural (flexural strength and flexural modulus) properties were measured at ambient conditions using a Universal Testing Machine (LR-50K, Lloyds Instrument, UK) as per the ASTM standards of D 638 and D 790, respectively, at a crosshead speed of 50 mm/min and 2.8 mm/min, respectively. Notched Izod impact strength was measured at ambient condition as per the ASTM standard of D 256 using an impact

**Table 1:** Prepared LLDPE/PXPEF formulations and their nomenclature.

Nomenclature	LLDPE (g)	PXPEF		Finalux G3	
		phr	g	phr	g
LLPX0	500.0	-	-	-	-
LLPX10	500.0	10.0	50.0	2	10
LLPX20	500.0	20.0	100.0	2	10
LLPX30	500.0	30.0	150.0	2	10
LLPX40	500.0	40.0	200.0	2	10

LLDPE=Linear low-density polyethylene,  
PXPEF=Pulverized cross-linked polyethylene foam

tester (Avery Denison, UK) with the striking velocity of 3.46 m/s, employing a 2.7 J striker. The notch for impact test was made using a motorized notch-cutting machine (Polytest Model 1, Ray Ran, UK).

### 3.2. VST

VST of the pristine LLDPE and PXPEF loaded LLDPE samples was measured using a VST Instrument (Davenport, UK). Specimens (dimension: 125 mm × 13 mm × 6.5 mm) were dipped in silicon oil bath and gradually heated at a constant rate of 2°C/min. The silicone oil was maintained under continuous circulation for having uniform temperature of the oil. A load of 1 kg was then applied over the specimen through the pin placed on the specimen; and the temperature at which the pin penetrates to a distance of 1 mm is noted as the VST. The entire operation was computer-controlled.

### 3.3. HDT

HDT of the pristine LLDPE and PXPEF loaded LLDPE samples was measured with an HDT Instrument (Davenport, UK). Specimen (dimension: 125 mm × 13 mm × 6.5 mm) was dipped in silicon oil bath, which had a 100 mm span for the sample, and was heated at a constant heating rate of 80°C/h. The oil was maintained under continuous circulation, for having uniform temperature of the oil. A load of 647 g was then applied over the specimen using a piston placed over it. The temperature at which the specimen deflects by a distance of 0.25 mm is noted as the HDT. Entire operation was computer-controlled.

### 3.4. MFI

The MFI, expressed as g/10 min, of LLDPE and LLDPE/PXPEF compositions was determined using an MFI instrument (Davenport, UK) at 190°C utilizing a load of 2.16 kg.

### 3.5. Rheological Property

A plot of melt viscosity (Pa.s) versus shear rate (s<sup>-1</sup>) for the LLDPE and LLDPE/PXPEF samples in lower shear rates (0.01-10/s) was obtained using a rotational rheometer (RT 10, Haake, Germany).

Equipped with a parallel plate assembly of diameter 35 mm at 230°C. Samples were pre-dried before analysis. Whereas, viscosity at higher shear rates (50 to 10,000/s) was obtained using a twin-bore capillary rheometer (Rosand Precision, UK) at the same temperature. The capillary had diameter of 1 mm and length of 16 mm, while the short capillary had  $L/D = 0$  with diameter same as that of long capillary which enabled the measurement of Bagley correction in measurement of extensional viscosity. Damping factor was determined against angular frequencies from 500/s to 0.5/s, at a constant temperature of 190°C. Rheological experiments were conducted under a nitrogen atmosphere to prevent oxidative degradation of the specimens.

### 3.6. Morphological Property

The morphological property of PXPEF loaded LLDPE samples was examined using a Scanning Electron Microscope (Cameca, France). A thin piece of specimen was etched with xylene for 12 h and coated with gold for enhanced conductivity. Xylene helped in dissolving the matrix LLDPE at the surface of the PXPEF/LLDPE sample.

## 4. RESULTS AND DISCUSSION

### 4.1. Mechanical Properties

Tensile, flexural, and impact properties obtained for pristine LLDPE and LLDPE/PXPEF compositions are tabulated in Table 2. Pristine LLDPE was found to have tensile strength, percentage elongation at break, flexural strength, flexural modulus, and impact strength values of 27 MPa, 90%, 12 MPa, 328 MPa, and 82 J/m, respectively. On the addition of PXPEF in LLDPE, the values of tensile strength and flexural strength decreased marginally, while that of percentage elongation at break and flexural modulus decreased drastically. However, an appreciable increase in the values of impact strength was observed. It can be seen that tensile strength, flexural strength, tensile modulus, and flexural modulus decreased by about 29, 25, 93, and 45%, respectively, while impact strength increased by about 380% for LLPX40 i.e., 40 phr PXPEF loaded LLDPE samples.

This trend observed in the tensile, flexural, and impact properties is attributed to the network structure formation by the PXPEF particles by its physical entanglement with the polymeric chains of LLDPE. This physical entanglement increases the gap between the LLDPE polymer chains, decreasing the number of polymer chains per unit area of the sample, thus decreasing its resistance to the applied tensile and flexural loads, leading to decrease in the tensile and flexural properties. This network structure also resists the molecular movements of LLDPE making it break the structure at lower elongations, thus decreasing the elongation at break property. However, when the samples were impacted, this network structure helped in enhanced transmission of the applied impact load through the molecular structure, increasing the impact load handling capability of the composition. Similar results have been reported by Miltz et al. [3] for the *in situ* ethylene methyl acrylate cross-linked blend of polypropylene and ethylene vinyl acetate. Thus, a physically cross-linked structure is formed on addition of PXPEF in LLDPE. The cross-linked structure is confirmed by scanning electron microscopy mentioned ahead.

### 4.2. VST, HDT, and MFI

Values of MFI, VST, and HDT determined for LLDPE and LLDPE/PXPEF compositions are reported in Table 3. Pristine LLDPE (LLPX0) was determined to possess MFI, VST, and HDT of 4.2 g/10 min, 121°C, and 40°C. These values decreased continuously with increased addition of PXPEF in LLDPE. For 40 phr PXPEF loaded LLDPE samples (LLPX40) MFI, VST, and HDT decreased to maximum possible extent by 98.8, 7.5, and 6.5%. Decrease in the values of VST and HDT was not much appreciable, however, MFI demonstrated a very appreciable decrease in its values as compared to pristine LLDPE (LLPX0). MFI is a measure of the flow property of the samples; while VST and HDT is a measure of the softness of the samples.

The observed trend in the values of MFI, VST, and HDT is in correlation with the mechanical properties explained in an earlier section. The “tentacles” of

**Table 2:** Mechanical properties obtained for LLDPE and LLDPE/PXPEF formulations.

Sample name	Tensile properties		Flexural properties		Impact strength (J/m)
	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	
LLPX0	27	900	12	328	82
LLPX10	23	264	11	280	102
LLPX20	23	116	10	260	157
LLPX30	21	86	10	210	197
LLPX40	19	63	9	180	394

LLDPE=Linear low-density polyethylene, PXPEF=Pulverized cross-linked polyethylene foam

the “spider”-like structure of the PXPEF particles physically inter-linked the polymeric chains of LLDPE forbidding them from undergoing molecular movements on application of heat or application of mechanical stress. The combined effect of these two, i.e., mechanical stress and temperature are demonstrated by MFI, VST, and HDT analysis. Increase in concentration of PXPEF in LLDPE brought about increased restrictions on the movement of the LLDPE.

Polymeric chains due to the increased physical cross-linking induced by the “spider”-like structure of the PXPEF. In MFI analysis, movement of LLDPE polymeric chains is restricted; whereas, in VST and HDT, decreased due to the increased distance between the LLDPE polymeric chains caused due to the physical presence of PXPEF, which made the structure softer to the applied stress; which was also the reason for the observed decrease in the mechanical properties. Thus, PXPEF added LLDPE samples will provide restriction to flow when applied with mechanical stress; but will be soft at lower temperature, with increased addition of PXPEF in LLDPE.

#### 4.3. Rheological Properties

Plot of melt viscosity (Pa.s) versus shear rate ( $s^{-1}$ ) obtained for pristine LLDPE and LLDPE/PXPEF is demonstrated in Figure 1. All the samples demonstrated nonlinear decrease in viscosity with an increase in shear rate, a typical behavior of shear-thinning materials. Melt viscosity of the samples increased with increase in concentration of PXPEF in LLDPE. Values of zero shear viscosity also increased with increased addition of PXPEF in LLDPE; however, all of them demonstrated similar viscosity values at very high shear rates due to the disruption of the molecular arrangement caused by the very high shearing force exerted by the rotating spindle of the rheometer. Addition of PXPEF into LLDPE induced a phenomenon of physical cross-linking into it restricting their molecular movements. This led to increased resistance of the material to the rotating spindle of the rheometer, demonstrating increased viscosity.

**Table 3:** VST, HDT and MFI obtained for the prepared samples.

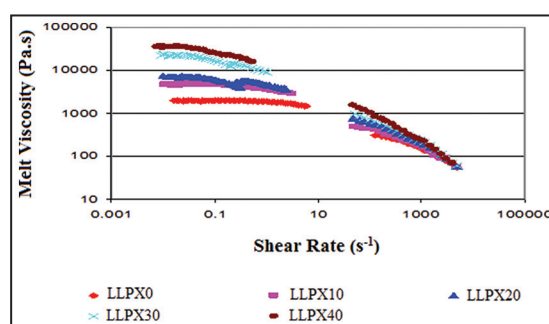
Sample name	MFI (g/10 min)	VST (°C)	HDT (°C)
LLPX0	4.2	121	40
LLPX10	2.0	118	39.2
LLPX20	1.1	117	38.7
LLPX30	0.4	115	38.3
LLPX40	0.05	112	37.4

VST=Vicat softening temperature, HDT=Heat distortion temperature, MFI=Melt flow index

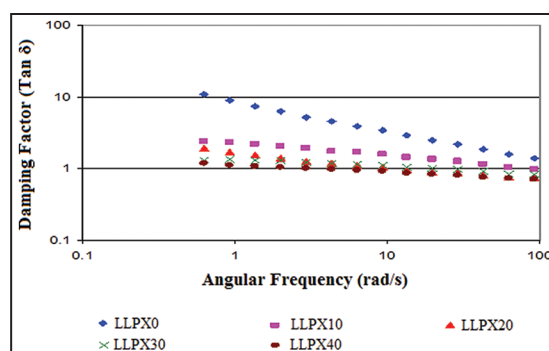
Damping factor is a measure of visco-elasticity of the polymer material. Damping factor is the ratio of loss modulus ( $G''$ ) to storage modulus ( $G'$ ). Higher values of damping factor indicate viscous nature of the polymer, while, lower values indicate elastic nature. Plot of damping factor (unitless) versus angular frequency (rad/s) obtained for pristine LLDPE and LLDPE/PXPEF samples is illustrated in Figure 2. It was observed that damping factor decreased with increased addition of PXPEF in LLDPE. Thus, the addition of PXPEF induced elasticity into LLDPE. This is caused due to the physical cross-linking induced by the addition of PXPEF into LLDPE. This led to the holding of the LLDPE polymer molecules together via the physical linkages by the PXPEF. Therefore, the addition of PXPEF induced elasticity into LLDPE polymer matrix. This increase in elasticity is the reason for the improvement observed in the impact strength of LLDPE on addition of PXPEF.

#### 4.4. Morphological Property

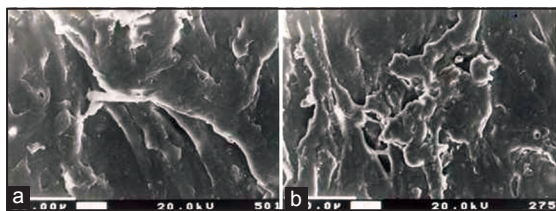
Scanning electron micrographs obtained for LLPX30 at a resolution of 50  $\mu m$  (a) and LLPX30 at a resolution of 100  $\mu m$  (b) are shown in Figure 3. The “spider”-like



**Figure 1:** Plot of viscosity versus shear rate obtained for linear low-density polyethylene (LLDPE) and LLDPE/pulverized cross-linked polyethylene foam formulations.



**Figure 2:** Plot of damping factor versus angular frequency obtained for linear low-density polyethylene (LLDPE) and LLDPE/pulverized cross-linked polyethylene formulations.



**Figure 3:** Scanning electron micrographs obtained for LLPX30 at a resolution of 50  $\mu\text{m}$  (a) and LLPX30 at a resolution of 100  $\mu\text{m}$  (b).

structure of PXPEF can be clearly seen in both a and b of Figure 3. In addition, the physical entanglements caused by it could also be observed in both A and B of Figure 3. This confirms the effect of PXPEF addition in LLDPE.

## 5. CONCLUSION

PXPEF added LLDPE compositions were successfully prepared using the processes of extrusion and injection molding. Concentration of PXPEF was added in varied concentration, 0, 10, 20, 30, and 40 phr, in LLDPE. Prepared compositions were characterized for mechanical, VST, HDT, rheological and morphological properties. Tensile strength, flexural strength, tensile modulus, and flexural modulus of 40 phr PXPEF added LLDPE composition decreased by 29, 25, 93, and 45%, respectively, while impact strength increased by about 380%. Melt flow index, VST and HDT also decreased appreciably with increased addition of PXPEF in LLDPE. Viscosity increased while damping factor decreased with increased addition of PXPEF in LLDPE, indicating an increase in elasticity of LLDPE by addition of PXPEF. All the observed trends in the mechanical, VST, HDT, and rheological properties

are attributed to the physical cross-linking induced by the “spider”-like structure of PXPEF into LLDPE.

## 6. ACKNOWLEDGMENT

Authors would like to acknowledge Institute of Chemical Technology (formerly UDCT) for permitting us to use the analytical facilities available at the Institute.

## 7. CONFLICT OF INTEREST

Authors declare no conflict of interest of any type.

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### \*Bibliographical Sketch



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