CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 ESCOR™ acid terpoymer

ESCOR™ terpolymers are trade name of polyethylene, poly(acrylic acid), and poly(methyl acrylate) copolymers. There are 3 grades of ESCOR™ terpolymers (ESCOR™ 310, ESCOR™ 320 and ESCOR™ 325) which are supplied by Exxon Chemical Company. ESCOR™ 310 terpolymer is a random terpolymer that consists of 87 %wt of ethylene, 6.5 %wt of acrylic acid and 6.5 %wt of methyl acrylate. It provides excellent adhesion to a variety of polar and non-polar materials. For example, ESCOR™ 310 can be used as an adhesive film for industrial laminations or to bond elastomers to fabrics and metals. It can also be used for extrusion coating/laminating and co-extrusion applications where bonding of polar to non-polar materials is critical. It delivers the highest service temperature and modulus of all the ESCOR™ acid terpolymer. It is used as heat-activated adhesive sealant compounds, TPOs with improved adhesion to metal parts, engineering thermoplastic impact modifier, and compatibilizer for polar and non-polar

ESCOR™ 320 terpolymer consists of 76 %wt of ethylene, 6 %wt of acrylic acid and 18 %wt of methyl acrylate. It provides excellent adhesion to a variety of substances and other film components, such as aluminum foil, polyolefin, polycarbonate, PET, etc. Applications for these terpolymers are tie resin for blown film, tie resin for extrusion coating and laminating, OPP/ESCOR™ 320/nylon laminates, and PE/ESCOR™ 320/aluminium foil laminates.

ESCOR™ 325 was employed. ESCOR™ 325 terpoymer consists of 74%wt of polyethylene, 20%wt poly(methyl acrylate) and 6.0%wt poly(acrylic acid). It provides excellent adhesion to a variety of polar and non-polar materials and also has the highest melt index and is the softest of all the ESCOR™ terpolymer. As a modifier, ESCOR™ 325 improves toughness, flexibility, and the adhesion characteristic of plastic compounds. Applications

of the terpolymer are engineering thermoplastic impact modifier, compatibilizer for dissimilar polymers, adhesion promoter for insert molded polyolefin parts, and heat activated seals.

Table 3.1 The characteristic of ESCOR™ acid terpolymers

Resin properties	**Test Based on**	Units (SI)	**Escor™ acid terpolymers**		
			310	**320**	**325**
Melt Index	Exxon Method	G/10min	6.0	5.0	20.0
Density	Exxon Method	g/cm3	0.941	0.953	0.950
Acid number	Exxon Method	Mg KOH/g	45	45	45
Peak melting temperature	Exxon Method	°F (°C)	201(94)	169(76)	163(73)
Peak crystalline temperature	Exxon Method	°F (°C)	165(74)	-	120(49)

3.1.2 EAA copolymers

EAA is an ethylene-acrylic acid random copolymer. Its attached functional groups provide specific interaction with other polymers. EAA copolymer is a soft, tough, transparent and similar to low density polyethylene (LDPE) at large elongation and low viscosity. EAA1-EAA5 copolymers supplied from the Exxon Chemical Company are used in this thesis.

Table 3.2 Compositions in mole fractions for four grades of EAA copolymers

Grade	Ethylene	Acrylic Acid
EAA1	0.988	0.012
EAA2	0.974	0.026
EAA4*	0.974	0.026
EAA5	0.961	0.039

*EAA4 has a lower molecular weigth than EAA2

3.2 Experimental Procedure

3.2.1 Polymer Blend Preparation

3.2.1.1 Blending

Blends of ESCOR™ 325 terpolymer and EAA copolymer (EAA1, EAA2, EAA4, and EAA5) were prepared at ratio of 0/100, 5/95, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10, 95/5, 100/0 by using a Collin co-rotating twin screw kneader ZK-25 (25mmx30D). Screw speed of 50 rpm was employed. All processing passes were carried out using the processing condition as shown in Figure 3.1.

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
125 °C	125 °C	127 °C	127 °C	130 °C	130 °C

Figure 3.1 Processing condition.

The extrudate was cooled in the water (~25°C) and cut into pellet form by a Planetrol 075D2 pelletizer.

3.2.2 Specimen Preparation

A sample was pressed on a Wabash V50H compression molding machine. The steps used in the process for this study were 160°C without pressure to preheat 8 minutes and 160°C with 15 tons force for 3 minutes. Mold was cooled down under pressure to 32°C. The mold used was a picture-frame type mode stainless steel

3.3 Characterization of Polymer-Polymer blends

3.3.1 Mechanical Properties

3.3.1.1 Tensile properties

Tensile properties such as Young's modulus, Tensile strength at break and Elongation at break were measured using an Instron Universal Testing Machine, Model 4206 ASTM-1708. At least five specimens per blend sample were tested using a crosshead speed of 130mm min^{-1}.

A. Young's modulus and tensile strength at break

Young's Modulus and Tensile strength at break were measured according to the ASTM D-1708 test procedure. The load cell of 100 kN and 200 mm/min cross-head speed were used for all tests. Dumbbell shape specimens were cut from compressed sheets using a pneumatic punch, and the specimen dimensions, were as follow: width of narrow section was 4.75 mm and the gauge length was 22.25 mm.

B. Elongation at break

Elongations at break were measured according to ASTM D-1708 test procedure. The load cell of 100 kN and 1.3 mm/min cross-head speed were used for all test specimens. Dumbbell shape specimens were cut from compressed sheets using a pneumatic punch, and the specimen dimensions, were as follow: width of narrow section was 4.75 mm and the gauge length was 22.25 mm.

3.3.1.2 Hardness

Hardness of the blends were measured using Durometer (ShoreD), according to ASTM D-2240. Thickness of specimens were 7.9 mm. The results were obtained from mean value of five measurements carried out on each sample.

3.3.1.3 Gloss

Gloss of the blends was measured using BYK Gardner Gloss-Haze Reflectometer at 20° and 60°, according to ASTM D-521. The results were averaged from five measurements on each sample to obtain a mean value.

3.3.2 Thermal Properties

3.3.2.1 Thermal properties of polymer blend

The thermal behavior of the ESCOR™ 325/EAAs blend samples was determined on a Perkin-Elmer DSC7. A sample of 9 ± 0.1 mg was sealed in clamped closed aluminum sample pans. Nitrogen gas was used as a purge gas. The heating and cooling program are as follow:

The sample was heated from 30°C to 140°C at heating rate of 80°C/min and cooled down to 30°C at cooling rate of 5°C/min and reheated it again from 30°C to 140°C at heating rate 5°C/min. The first heating scans were carried out to erase any thermal history of the sample and the melting temperature (T_m), Enthalpy of fusion (ΔH_f) were collected from thermogram of the second scan.

3.3.3 Crystallization

3.3.3.1 Crystallization structure

X-ray diffraction patterns of all ESCOR™ 325/EAAs blends were obtained using a Rigaku Rint2000 diffractometer equipped with a graphite monochromator and a Cu tube for generating a CuKα radiation (1.5046 A). First,

the sheet samples were erased their history of polymers using DSC at heating rate 5°C/min. Then, the sheet sample was put on a glass slide specimen holder using vasaline as binder between sample and glass holder. The specimen was examined between 5°-35° 2θ at a scanning rate of 2° 2θ /min in 0.02° 2θ increments. CuKα radiation with λ = 0.154 nm. was used as the X-ray source and operated at 40 kV and 30 mA. The digital output of the proportional X-ray detector and the gonimeter angle measurement was sent to an online microcomputer for storing the data.

The XRD patterns of the crystalline and amorphous scattering in the diffraction pattern were separated from each other and were used for determination the degree of crystallinity. The degree of crystallinity (χ_c) is equal to the ratio of the crystalline scattering area to the total scattering area, both crystalline and amorphous.

3.3.3.2 Crystallization behavior

A Perkin-Elmer Series 7 Differential Scanning Calorimeter (DSC7) was use to follow nonisothermal and isothermal crystallization of 3 different grades of ESCOR™ acid terpolymer and Ethylene acrylic acid copolymers (EAA1-EAA5). Temperature calibration was performed using indium as a standard that has the thermal properties; T^o_m = 156.6°C and $\triangle H^o_f$ = 28.5 J g^{-1}. The consistency of the temperature calibration was check every other run to ensure reliability of the data obtained. Samples of mass 9 ± 0.1 mg were sealed in DSC pans. Nitrogen gas was used as a purge gas.

In the nonisothermal experiment, the samples were heated from 30°C at scanning rate of 80°C min^{-1} to 150°C, and were held at 150°C for 5 min before cooling at a desired constant cooling rate, ranging from 5 to 50°C min^{-1}.

3.3.4 Rheological Measurement

Pellets of polymer blends of ESCOR™ 325/EAAs were compressed into circular disk of 1-mm thickness. An ARES Rheometric Dynamic Analyzer RDA-II with cone-and-plate geometry was used for measuring rheological properties, storage modulus, loss modulus and tan δ. Measurements were carried out at 130°C and to

make sure that the behavior of the test specimens were in linear viscoelastic range, frequency and strain amplitude were varied in the range between 0.1 to 100 rad/s to obtain a suitable range of the torque. This value, higher than the melting temperature of each polymer blends, was chosen a allow adequate duration of the experiments without noticeable degradation.

3.3.5 Dynamic Mechanical Properties

The dymamic mechanical properties of ESCOR^{TM} 325/EAAs were measured with Solid Analyzer RSAII (Rheometric Scientific provided the storage modulus (E'), loss modulus (E") and tan δ. Film and fiber fixture was used to mount the samples and 3K temperature steps were used. All experiments were measured with a frequency of 10 rad/s and a strain rate of 0.1% and with static force tracing dynamic force. The temperature range studied was from –150°C to 150°C and the sample was heated at rate of 10°C/min.