CHAPTER 3 - EXPERIMENTAL TECHNIQUES

3.1 INTRODUCTION

The general transesterification reaction between two esters is defined as follows:

$$RCO_2R'' + R'CO_2R''' \Leftrightarrow R'CO_2R'' + RCO_2R'''$$

Transesterification is a generic term applied to a collection of intermolecular reactions and includes alcoholysis, acidolysis, and ester interchange. In the presence of an organic acid, polyester may undergo acidolysis, reducing the molecular mass. In the special case of alcoholysis the reaction is between an ester and an alcohol:

$$RCO_2R'' + R'''OH \Leftrightarrow R''OH + RCO_2R'''$$

The alcoholysis reaction is an exchange of the alcohol of the ester with another alcohol to form a new ester.

Transesterification reactions take place readily between polyesters such as polymethacrylate and polycarbonate, polyethylene terephthalate (PET) and polycarbonate and polymethacrylate with polyethylene terephthalate (PET) [67]. The analogous reaction in polyamides is termed transamidation. Since reaction time influences the transesterification reaction [74], the method used for processing also has an influence on the transesterification.

3.2 MATERIALS

Table 3.1 lists the materials used as additives in this study. Unstabilised samples of low-density polyethylene (LDPE) and polypropylene homopolymer were obtained from Polifin. Commercially stabiliser additives were masterbatched (10% actives level by mass) into MFI polyethylene resin on a laboratory extruder. For the other additives, high speed mixing was used to incorporate them into the polymer resin in powder form.

The first four compounds listed in Table 3.1 are hindered amine stabilisers with available alcohol functionality. They are too volatile to use as light stabilisers. Esterification and transesterification reactions were therefore employed to increase their effective molecular mass.

According to Ligner and Malik [54] the key requirements for an effective UV stabiliser are (1) high solubility, (2) minimal diffusion and (3) high homogeneity in the distribution of the additive. The HALS radicals, **TA**, **TOL**, **MA** and **DIOL**, are highly polar whereas polyethylene and polypropylene are highly non-polar. In an attempt to satisfy requirement (1), we invoke the principle of "like dissolves like". We used polyesters and stearic acid as co-reactants. The long alkyl chain of stearic acid (≡ **STE**) is similar in structure to polyethylene and should improve solubility in both polyethylene and polypropylene. Esters feature relatively low polarity as is attested by the corresponding low polarity of ester-based solvents. In order to satisfy the low mobility requirement (2), we tried to synthesize oligomers with reasonably high molecular masses of the order of 2000 Daltons. Requirement (3) should be satisfied, provided requirements (1) and (2) are met, and if good dispersion of additive is ensured during processing.

In order to simplify synthesis we opted to react the additives into high molecular mass polyesters such as polycaprolactone (grade 767 ex Union Carbide ≡ **TO**) and polybutylene succinate (grade Bionolle # 1001 ≡ **BU**).

Table 3.1 Compounds used as additives

Abbreviations	*Name of additives*	*CAS No.*	*Suppliers**
TA	2,2,6,6-Tetramethyl-4-piperidinol (TAA-OL)	[2403-88-5]	1
TOL	4-Hydroxy-2,2,6,6-Tetramethyl –Piperidin-1-Ethanol (N-HE-TAA-OL)		1
MA	1,2,2,6,6-Pentamethyl-Piperidin-4-0L (N-METHYL-TAA-OL)		1
DIOL	2,2-(2,2,6,6-Tetramethyl-4-piperidinyl)imino)bis (Ethanol)		1
Fe Acac	Iron (III) 2,4-pentanedione	[14024-18-1]	2
Ti Acac	Titanyl 2,4-pentanedione	[14024-64-7]	3
Zir Acac	Zirconium (IV) 2,4-pentane dione	[17501-44-9]	3
Mg Acac	Magnesium 2,4-pentanedione	[68488-07-9]	2
Va Acac	Vanadyl 2,4-pentanedione	[3153-26-2]	2
Cu Acac	Copper (II) 2,4-pentanedione	[13395-16-9]	3
Ca Acac	Calcium 2,4-pentanedione	[19372-44-2]	2
Al Acac	Aluminum 2,4-pentanedione	[13963-57-0]	2
Fe-Stea	Iron (III) Stearate	[2980-59-8]	-
Phetln	Phenolphtalein	[77-09-8]	3
Ni-Dmg	Nickel dimethyl glyoxime	[13478-93-8]	-
OTMQ	Poly (1,2 – dihydro – 2,2,4 – trimethylquinoline)	[26780-96-1]	-
Anox 20	Tetrakis methylene (3.5-di-t-butyl-4-hydroxy hydrocinnamate) methane		-

* 1. Creanova; 2. Aldrich; 3. Merck- Schuchardt

3.3 SYNTHESIS OF UV STABILISERS

The reactor consisted of a three neck round-bottomed flask, having a capacity of one litter, fitted with a condenser. The three openings allowed the insertion of a thermometer, connection with a reflux condenser and the collection of solvent. In order to form a homogeneous solution between UV stabilisers and the polymers, an appropriate solvent was added. The following solvents were used: Toluene, acetone and chloroform. Tetrabutylorthotitanate [($C_{16}H_{36}O_4$)Ti] obtained from Merck-Schuchardt was used as catalyst. All the chemicals used in the experiments were of analytical grade.

3.3.1 HALS BASED ON OLIGOMERIC POLYESTERS.

The polymers and the UV stabilisers were dissolved in an appropriate solvent and the mixture was heated at reflux for several hours. After the reaction was deemed complete the mixture was removed from the reactor. The solvent was then removed from the product using roto-evaporation. The final product was finally washed with distilled water and dried at room temperature.

3.3.1.1 SYNTHESIS OF STETA

We have used the transesterification reaction of secondary alcohol with aliphatic carboxylic acids to prepare 4 - stearoyloxy- 2,2,6,6 – tetramethylpiperidine (STETA).
The overall reaction can be written as:

$$C_{18}H_{36}O_2 + C_9H_{19}NO \Rightarrow C_{27}H_{53}O_2N + H_2O \qquad [1]$$

	$C_{18}H_{36}O_2$	$C_9H_{19}NO$	$C_{27}H_{53}O_2N$	H_2O
Mm (g/mol)	284.48	157.24	423.72	18
Mass used (g)	45.3	25		
Mass expected (g)			67.43	

Stearic acid dissolved readily in toluene at room temperature, but TAA-OL was dissolved in toluene only at high temperature (80°C). The mixture of 45.3 g (0.159 mol) of stearic acid, 25 g (0.159 mol) of TAA-OL and 150.14 g of toluene as solvent was heated at reflux (105 °C) for 28h30'. In order to accelerate the reaction, tetrabutylorthotitanate (1%) was used as catalyst. Toluene was removed using roto-evaporation. The residue was poured into 750 ml of acetone and filtered. The acetone was evaporated and the residue was dissolved in 170 g of hexane and extracted three times with distilled water to remove catalyst residues. The hexane solution was dried by anhydrous sodium sulphate. By cooling the hexane solution, a white powder was obtained as the final product (yield 87.3 %). The theoretical elemental analysis for $C_{27}H_{53}O_2N$ was C:N = 23.2, while it was found to be C:N = 20.7.

3.3.1.2. SYNTHESIS OF TOTOL

The transesterification reaction between N-hydroxyethyl triacetone amino alcohol with caprolactone can be expressed by the following equation:

$$\mathbf{C_{11}H_{23}NO_2 + 5\ C_6H_{10}O_2 \Rightarrow C_{41}H_{63}O_7N + 5\ H_2O} \qquad [2]$$

Mm (g/mol)	201.3	114.13	681.95	18
Mass used (g)	12.3	35		
Mass expected (g)			41.78	

From preliminary work it was found that N-hydroxyethyl triacetone amino alcohol did not dissolve in toluene but it dissolved in acetone. On the other hand, caprolactone did not dissolve in acetone but it dissolved in toluene. Since toluene and acetone were miscible, N-hydroxyethyl triacetone amino alcohol and caprolactone were dissolved respectively in acetone (300 g) and toluene (300 g), and the two solutions were mixed later. The solution (caprolactone and Toluene) was put in a tumbler mixer for 24 hours to allow the caprolactone to be completely dissolved in toluene. On the other hand, N-hydroxyethyl triacetone amino alcohol was dissolved in acetone after stirring for thirty minutes at room temperature. The mixture was then heated up to the boiling point of the solution (65 °C) for 24h 18'. The vapour was recycled after condensation during the experiment. Tetrabutylortotitanate (1%) was used as catalyst. The final product was separated from the solvent by using the roto-evaporator and yielded 82.3% of a gelatinous product after cooling to room temperature. The theoretical elemental analysis for $C_{41}H_{63}O_7N$ was C:N = 35.2; the following value was found C:N = 33.5.

3.3.1.3 SYNTHESIS OF TOTA

The transesterification reaction between triacetone amino alcohol with caprolactone can be expressed by the following equation:

$$\mathbf{C_9H_{19}NO + 5\ C_6H_{10}O_2 \Rightarrow C_{39}H_{59}O_6N + 5\ H_2O} \qquad [3]$$

Mm (g/mol)	157.24	114.13	637.89	18
Mass used (g)	8.3	35		
Mass expected (g)			37.95	

Toluene (300 g) was used to dissolve the two reactants and the mixture was heated up to 105 °C for 23h 40'. The same procedure as described previously was used to obtain the final product. The residue was separated from the solvent by using the roto-evaporator and yielded 81.7% of a gelatinous product after cooling at room temperature.

Tetrabutylorthotitanate (1%) was used as catalyst. The residue formed a viscous solution with the solvent, which did not allow a good separation. The theoretical elemental analysis for $C_{39}H_{59}O_6N$ was C:N = 33.5; that found was C:N = 35.0.

3.3.1.4 SYNTHESIS OF BUTA

The transesterification reaction between triacetone amino alcohol with polybutylene succinate can be expressed by the following equation:

$$\mathbf{C_9H_{19}NO + 5\ C_8H_{12}O_4 \Rightarrow C_{49}H_{69}O_{16}N + 5\ H_2O} \quad [4]$$

Mm (g/mol)	157.24	172.17	928.09	18
Mass used (g)	9.13	50		
Mass expected (g)			53.9	

600 g of Chloroform was used to dissolve the two reactants. Tetrabutylorthotitanate (1%) was used as catalyst. The mixture was refluxed at 58 °C for 20h 45'. The reaction mixture was rotor-evaporated and yielded 81.6% of a white powder. The theoretical elemental analysis for $C_{49}H_{69}O_{16}N$ gave C:N = 42.0; while it was found to be C:N = 44.3.

3.3.1.5 SYNTHESIS OF BUTOL

The transesterification reaction between N-Hydroxyethyl triacetone amino alcohol with polybutylene succinate can be expressed by the following equation:

$$\mathbf{C_{11}H_{23}NO_2 + 5\ C_8H_{12}O_4 \Rightarrow C_{51}H_{73}O_{17}N + 5\ H_2O} \quad [5]$$

Mm (g/mol)	201.3	172.17	972.15	18
Mass used (g)	11.7	50		
Mass expected (g)			56.47	

600 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated up to 58 °C for 20h 15'. The final product was separated from the solvent by using the roto-evaporator and yielded 88.7% of a white

powder. The theoretical elemental analysis for $C_{51}H_{73}O_{17}N$ was C:N = 43.8; the following value was found C:N = 38.5.

3.3.1.6 SYNTHESIS OF BUMA

The transesterification reaction between N-methyl triacetone amino alcohol with polybutylene succinate can be expressed by the following equation:

$$\mathbf{C_{10}H_{21}NO + 5\ C_8H_{12}O_4 \Rightarrow C_{50}H_{71}O_{16}N + 5\ H_2O} \qquad [6]$$

Mm (g/mol)	171.28	172.17	942.13	18
Mass used (g)	10	50.3		
Mass expected (g)			55.04	

456.5 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated up to 58 °C for 27h 10'. The final product was separated from the solvent by using the roto-evaporator and yielded 87.6% of a white powder. The theoretical elemental analysis for $C_{50}H_{71}O_{16}N$ was C:N = 42.9; while it was found to be C:N = 37.2.

3.3.1.7 SYNTHESIS OF BUDIOL

The transesterification reaction between 2,2-(2,2,6,6-Tetramethyl-4 Piperidinyl) imino) bis (Ethanol) with Polybutylene succinate can be expressed by the following equation:

$$\mathbf{C_{13}H_{28}N_2O_2 + 5\ C_8H_{12}O_4 \Rightarrow C_{53}H_{78}O_{17}N_2 + 5\ H_2O} \qquad [7]$$

Mm (g/mol)	244.38	172.17	1015.23	18
Mass used (g)	15	52.5		
Mass expected (g)			62	

360.3 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated up to 59 °C for 28h 20'. The final product was separated from the solvent by using the roto-evaporator and yielded 93.4% of a white powder. The theoretical elemental analysis for $C_{53}H_{78}O_{17}N_2$ was C:N = 22.7; the value found was C:N = 19.5.

3.3.1.8 SYNTHESIS OF STEMA

The transesterification reaction between N-Methyl triacetone amino alcohol (N-METHYL-TAA-OL) with stearic acid can be expressed by:

$$\mathbf{C_{10}H_{21}NO + C_{18}H_{36}O_2 \Rightarrow C_{28}H_{55}O_2N + H_2O} \qquad [8]$$

Mm (g/mol)	171.28	284.48	437.76	18
Mass used (g)	27.2	45.2		
Mass expected (g)			69.54	

350 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated up to 60 °C for 25h 50'. The final product was separated from the solvent by using the rotor-evaporator and yielded 90.5% of a white powder. The theoretical elemental analysis for $C_{28}H_{55}O_2N$ was C:N = 24.0; while it was found to be C:N = 22.7.

3.3.1.9 SYNTHESIS OF STEDIOL

The transesterification reaction between 2,2-(2,2,6,6- tetramethyl 4-piperidinyl) imino) bis (ethanol) with stearic acid can be expressed by :

$$C_{13}H_{28}N_2O_2 + 2\ C_{18}H_{36}O_2 \Rightarrow C_{49}H_{96}O_4N_2 + 2\ H_2O \qquad [9]$$

Mm (g/mol)	244.38	284.48	777.34	18
Mass used (g)	24.4	56.9		
Mass expected (g)			77.7	

330 g of Chloroform was used to dissolve the two reactants and tetrabutylorthotitanate (1%) was used as catalyst. The mixture was heated at 60 °C for 28h35'. The final product was separated from the solvent by using the rotor-evaporator and yielded 88.3% of a white powder. The theoretical elemental analysis for $C_{49}H_{96}O_4N_2$ was C:N = 21.0; the following value was found to be C:N = 22.6.

3.3.2 METAL COMPLEXES

Ferric stearate was prepared as follows. Potassium hydroxide (0.165 mol) was dissolved in 1 litre of distilled water. A total of 46.94 g (0.165 mol) stearic acid was added in small portions while stirring. The next quantity was only added upon complete dissolution of the previous quantity. To this solution was added a total of 26.94 g (0.055 mol) ferric sulphate pentahydrate. The resultant precipitate was recovered by filtration. The filter cake was washed with copious quantities of distilled water to remove the soluble potassium sulphate. The product was dried for 24 hours at 60°C in a convection oven. The yield was 48.6 g (96.7%).

Nickel dimethyl glyoxime was prepared as follows. 20.92 g of sodium salt (0.06877 mol) was used. 20% excess of sodium salt (25.11 g) was dissolved in 1 litter of water. 20 g of nickel salt was completely dissolved in water also. The sodium salt was added upon complete dissolution of the nickel salt solution. The solution forms a pink precipitate immediately that was recovered by filtration. The filter cake was washed with an excess of distilled water and latter with hexane. The product was dried for 21 days in a dessicator. The yield was 93.5%.

3.4 ANTI-OXIDANT PROPERTIES

The oxidation induction temperature (OIT) was used to determine the effect of the additives on the thermal stability of the polymers. OIT's were obtained by Differential Scanning Calorimetry (DSC) on a Perkin Elmer DSC 7 at a scan rate of 2°C/min in a stream of air or at a scan rate of 10°C/min in oxygen flowing at 20 ml/min.

The effect of some additives on the process stability of the polymers was also evaluated using the method of repeated extrusion. The experimental procedures and conditions were as follows.

POLYPROPYLENE. Grade 1100K unstabilised homopolymer powder, ex Polifin, with a nominal MFI of 3.5 g/10 min @ 230°C/2.16 kg, was used. Test mixtures were prepared by dry blending the polypropylene powder with the required amount of stabilisers in a coffee grinder. The standard recipe was 0.2% calcium stearate together with 0.1% antioxidant blend. These mixtures were then extruded directly.

POLYETHYLENE. Since oxidative degradation initially leads to an increase in melt viscosity, it was decided to use LDPE grade WNG 14 ex Polifin. The initial melt flow index of this resin was 7.0 g/10 min @ 190° C/2.16 kg. In this case 0.1% stabiliser blend was incorporated via the 10% masterbatches. No calcium stearate was used with the polyethylene.

3.5 CHARACTERISATION OF ADDITIVES

3.5.1 THERMAL ANALYSIS (DSC/TGA)

The spectra of all products are attached as Appendix A. A Perkin Elmer DSC 7 instrument was used to collect calorimetric data. Sample masses of approximately 10±1 mg were weighed into aluminium pans. Air was used as a dynamic atmosphere with a flow rate of approximately 20 ml/min.

A Netzsch STA 409 simultaneous TG/DSC instrument was used to collect thermogravimetric and calorimetric data. Sample masses of approximately 10±1 mg were weighed into aluminium pans. Air was used as a dynamic atmosphere with a flow rate of approximately 20 ml/min.

3.5.2 SPECTROSCOPIC CHARACTERISATION (UV)

IR spectra were obtained using pressed KBr pellets. The spectra of all the products are attached as Appendix B. Mid-infrared absorption spectra were recorded of the additives in a Bruker® 113V FTIR spectrometer. The sample chamber of the instrument was evacuated during the recordings to minimise any effects caused by water vapour and carbon dioxide. The resolution was 2 cm^{-1} and 32 scans were signal-averaged in each interferogram.

3.5.3 ELEMENTAL ANALYSIS

Elemental analysis of UV stabilisers for C and N were performed by the Agricultural Research Council.

3.6 CHARACTERISATION OF FILM

Films were obtained by using a laboratory film blower. High speed mixing was used to incorporate additives (different dosage level was used) into the polymer resin in powder form. 0.05% of Anox 20 was added to all additives synthesized.

The additives TOTOL and TOTA were gelatinous products. To incorporate them into the polymer resin, they were first dissolved in chloroform. This solution was poured into polymer resin for good mixing. The resultant mixture was then dried for 14 days in room temperature to remove chloroform.

3.6.1 UV TEST

In order to evaluate the performance of metal 2,4-pentanedione complexes, anti-oxidants and ferric stearate compounded in polyethylene and polypropylene films in UV, UV-VIS purge trials were performed. A single layer of each film mounted at right angles to the light path in calibrate UV-VIS spectrophotometer [Spectronic genesys 5 (Beack = 4.00 and O = 0.006)] and scanned from 700 to 400 nm.

3.6.2 ACCELERATED UV AGEING

Low-density polyethylene (MFI 2,0) and polypropylene film samples (MFI 1,8) were blown on a laboratory film blower. The ca. 40 µm thick films samples were weathered in a QUV fitted with A340 UV lamps for up to 2900 hours. A dry cycle was used with the temperature set at 45°C.

Mid-infrared absorption spectra were recorded of the samples mounted on plastic squares to fit into the sample holder of a Bruker® 113V FTIR spectrometer. The sample chamber of the instrument was evacuated during the recordings to minimise any effects caused by water vapour and carbon dioxide. The resolution was 2 cm^{-1} and 32 scans were signal-averaged in each interferogram.

The recorded spectra were baseline corrected. The Carbonyl Index [12] used here was defined as the ratio of the intensities of the C=O band at 1710 cm^{-1} to the C-H rocking band at 729 cm^{-1} for polyethylene films and the band at 972 cm^{-1} for polypropylene films. The latter peaks remained unchanged during the degradation process. In our study the C-H stretch vibration band at 2820 cm^{-1} could not be used as the film thickness of the samples was sufficient to cause the intensity of this band to be so high that it was cut off, i.e. it was saturated. A specific fixed Carbonyl Index value may be used to define a failure criterion for use in photo-stabilisation studies of polymers. A value of CI = 0.1 in this study.