# DETERMINATION OF SOME PROPERTIES OF BLENDS OF POLYSTYRENE AND MODIFIED EPOXIDIZED SOYBEAN OIL RESINS

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DEPARTMENT OF CHEMISTRY,

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FEBRUARY, 2017

## DECLARATION

I declare that the work in this dissertation entitled "DETERMINATION OF SOME PROPERTIES OF BLENDS OF POLYSTYRENE AND MODIFIED EPOXIDIZED SOYBEAN OIL RESINS" has been performed by me in the Department of Chemistry under the supervisions of Dr. P.A.P Mamza and Dr. A. Ejila. The information derived from the literature has been acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another Degree or Diploma at any other University.

| | | |
|---|---|---|
| IGBOZURUIKE CHIDIEBERE COLLINS | …… | …… |
| Name of Student | Signature | Date |

## CERTIFICATION

This dissertation entitled "DETERMINATION OF SOME PROPERTIES OF BLENDS OF POLYSTYRENE AND MODIFIED EPOXIDIZED SOYBEAN OIL RESINS" by IGBOZURUIKE CHIDIEBERE COLLINS meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation

| | | |
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## ABSTRACT

Soybean oil is among the most abundant, biodegradable, renewable and sustainable vegetable oil in Nigeria that is rich in polyunsaturated fatty-acids, which earned a good candidate for epoxidaton. However, the epoxidized soybean oil (ESO) alone lacks good thermo-mechanical properties. Therefore, ESO is synthesized, thermally pre-cured and finally cured with polystyrene to obtain a blend of good thermo-mechanical properties. The soybean oil sample was subjected to FT-IR spectroscopy to determine the characteristic bands of functional groups, and then analyzed to determine the number of carbon-carbon double bond(s) present in 100g of the oil sample. The result indicated 149.8 as the iodine number. The resultant/determined number of carbon-carbon double bonds was interpreted in terms of molar equivalent and then stoichiometrically combined with peracetic acid (formed in-situ) to yield 9.77% oxirane-oxygen content of the soybean epoxy resin. The resin was subjected to Fourier Transform Infra-Red (FT-IR) spectroscopy within the frequency range of (400-4000) cm-1. The observable peaks showed a characteristic band of 843cm-1, 823cm-1 903cm-1 corresponding to internal, external and terminal oxirane-oxygen rings respectively, with disappearance at peak 3008 and 914 cm-1 at cis- and trans-, di-substituted olefins in soybean oil sample. The epoxidized soybean oil (ESO) was cured thermally to yield a gel coded as modified epoxidized soybean oil (MESO). The MESO was subjected to FT-IR, and the characteristic bands obtained indicated 3400cm-1and above. The MESO was blended with polystyrene in the ratio of 10/0, 9/1, 8/2, 7/3, 6/4, 5/5, 4/6 PS/MESO respectively. The mechanical properties of the blend were studied and the results indicated that 6/4 blend of PS/MESO gave highest values of tensile strength (4.3 x 105 Nm-2) and Young's modulus(14.9 x 105 Nm-2) and a lower value of elongation at break 29%. Viscometric study of the blends were carried out and the results affirmed that the blend at 6/4

PS/MESO composition gave the additive value of R2 from both relative and reduced viscosity measurements respectively. The study showed that thermally cured resin of soybean oil is compatible with polystyrene and thus, at 6/4 PS/MESO composition, serves as reinforcement to polystyrene matrix.

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# LISTS OF ABBREVIATIONS

| | |
|---|---|
| AOCS | American Oil Chemists Society |
| ASTM | American Standards for Testing Materials |
| ESO | Epoxidized Soybean Oil |
| FT-IR | Fourier Transform Infra Red spectroscopy |
| MESO | Modified Epoxidized Soybean Oil (thermally cured soybean oil epoxy resin) |
| NA | Not Available |
| PS | Polystyrene |
| PMMA | Poly (methyl methacrylate) |
| SPR | Structure Property Relationship |
| QSAR | Quantitative Structure Activity Relationship |
| LOE | Leen Oil Epoxyl |
| TAG | Tri-Acyl Glycerol |
| DGEBA | Di-Glycidyl Ether of Bisphenol A |
| HDGEBA | Hydro, Di-Glycidyl Ether of Bisphenol A |
| PPO | Poly (phenylene oxide) |
| PPE | Poly (phenylene ether) |
| PET | Poly (ethylene terephthalate) |
| PBT | Poly (butylene terephthalate) |

# CHAPTER ONE

## 1.1 INTRODUCTION

Vegetable oils are agricultural products derived from the seeds of many plants such as soybean, castor, neem, rubber, coconut, melon, jatropha, palm, olive oil trees e.t.c. Different plant seeds contain different volume of vegetable oil per kilogram of seeds' weight. Within the same plant seeds, the difference in species of seeds also gives rise to difference in the volume of vegetable oil per kilogram of that species.Vegetable oils contain triglyceride molecule. Other constituents of vegetable oils include; tocopherol, lignins, and vitamin E. Generally, all vegetable oils contain the same molecular morphology of triglyceride in terms of shape but different in fatty-acids composition and distribution within the triglyceride molecule. The end-use applications of vegetable oils in foods, cosmetics, pharmaceuticals, polymer industries e.t.c. depend (among other factors) on the difference in fatty-acids composition and distribution within the triglyceride molecule. This is an optimization technique often referred as structure-property relationship (SPR) or quantitative structure activity relationship (QSAR). Based on this technique, vegetable oils are classified as; edible and non-edible, drying, semi-drying and non-drying. Vegetable oils in their raw-form, may find direct end-use application, or may need refining or chemical modification for better end-use application, all depending on the physicochemical property of interest and engineering design. Chemical modification such as epoxidation can serve as a precursor route for synthesis of bio-based industrial chemicals such as glycols, lubricants, plasticizers, stabilizers e.t.c,(Tayde*et al* 2012).

For an example, in an engineering design aimed at end-use properties of plasticization and stabilization for application in polymer industry, vegetable oils may be subjected to chemical or/and chemo-physical modification such as epoxidation, cationic polymerization, copolymerization or blending with petro-chemical product.Epoxidized vegetable oil such as epoxidized soybean oil (ESO) resin, has disappointing thermo-mechanical properties for practical applications in terms of load bearing capacity.Park *et al* (2003) synthesized epoxy resin from soybean oil and castor oil and found that glass transition temperature was less than $50^0$C.Javni*et al*(2004) prepared polyurethane foam from soybean oil derivative and the result indicated that the useful thermo-mechanical properties of the oil base resin were depended strongly on incorporation of rigid petroleum product, especially when the rigid content was 50% and above.Sharif *et al* (2001) used Differential Scanning Calorimetry (DSC) to determine the glass transition temperature of leen seed oil epoxy/polystyrene polyblend, and found that only single $T_g$was observed indicating homogenous miscibility of constituents of the blend at all ratios.Mamza and Folaranmi(1996) also found that polystyrene and polyvinylacetate were miscible in both polar and non-polar solvents such as chlorobenzene, tetrahydrofuran and toluene.Ashrat*et al*(2007) observed that the tensile strength, as well as elongation-at-break increased with increasing polystyrene content in leen seed oil epoxy/polystyrene (LOE/PS) polyblend. Thus, LOE increases flexibility and plasticity of polystyrene enormously. The blend structure shows the tensile strength behaviour similar to low-density polyethylene.Therefore, to obtain acceptable thermo-mechanical properties for practical application especially in terms of load bearing capacity, the epoxidize soybean oil should be modified either by copolymerisation, blending or reinforcement.

Cationic polymerization of double bonds of triglyceride molecule gives a very low molecular weight polymer with the subsequent attendance poor thermo-mechanical properties, resultantly unsuitable for an engineering design aimed at end-use properties of tensile strength, thermal stability and good processing temperature for application in polymer industries.Thus, vegetable oils alone, despite its merits such as biodegradability, eco-friendliness, sustainability, renewability e.t.c against the petroleum products(crude oil) counterpart and cannot be used to achieve satisfactory thermo-mechanical properties.Therefore, progression is on-going in compromising both merits and demerits of vegetable oil and crude oil respectively for suitable end-use properties and applications

## 1.2 RESEARCH PROBLEM/BACKGROUND OF THE STUDY

### Local Content Utilization and Diversification

Most industrial raw materials used in Nigeria polymer industries are petroleum products. Most of these petro-based raw materials such as epoxides are imported. Thus, foreign currencies are needed to source these raw materials which consequently mount pressure on local currency with attendant devaluation. However, since fossil fuel depletes with time amidst its demerits such as non-biodegradability, environmental hazards, and high cost, efforts are in progress to reduce crude oil dependence for revenue generation as well as industrial based raw-materials due to its negative effect on climate change. Thus, agricultural products which are sustainable, biodegradable, renewable and low cost, offer a promising alternative to crude oil. Thus, an agricultural product, such as vegetable oils can be diversified into many industrial raw-materials (e.g epoxides) amidst its domestic usages

## 1.3 JUSTIFICATION OF THE STUDY

Among many monetary policies of Central Bank of Nigeria to remedy the foreign exchange cisis, is the direct U.S dollar sell to manufacturers under the umbrella of Manufacturing Association of Nigeriato boast productivity and reduce the resultant pressure effect on Naira. However, thesemonetary policies have not yielded the expected results as dollar demand continued on increase amidst its paucity with subsequent devaluation of Naira and resultant economic recession. Thus, epoxyl resins of soybean oil as a precursor for synthesis of many industrial chemical products will not only reduce U.S dollar demand for industrial chemical products to safe Naira, but also increases the gross domestic products andreduces environmental hazards associated with petroleum products.

## 1.4 SCOPE (LIMITATION) OF THE STUDY

High cost and non-availability of some chemical reagents within Zaria limits furtherstudy on the conversion of the oxirane-oxygen to other functional groups.

## 1.5. AIM AND OBJECTIVE OF THE STUDY

The aim of the study is to produce and determine the compatibility of blends of thermally cured epoxyl resin of soybean oil with polystyrene.

The specific objectives of the study are to:

(i) Determine the iodine number of soybean oil.

(ii) Epoxidize the soybean oil and thermal curing of epoxidized soybean oil (MESO).

(iii) Produce varying blends of polystyrene and MESO.

(iv) Determine the viscosity and mechanical properties (Young's modulus, tensile strength and elongation-at-break) of blends and access the compatibility of the blends.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.0. SOYBEAN OIL

Soybean oil is among the most aboundantedible vegetable oil in tropical Africa that is rich in polyunsaturated fatty-acids. The Structure of triglyceride molecule of soybean oil and its fatty acid distribution are shownin fig. 2.1, and section 2.1 respectively(Gunstone, *1996*) and (Liu, 1997).

Fig. 2.1. Structure of triglyceride molecule of soybean oil.

## 2.1THE FATTY ACIDS DISTRIBUTION IN SOYBEAN OIL IS AS FOLLOWS:

(i) 53.2% linoleic acid

(ii) 23.4% oleic acid

(iii) 7.8% linolenic acid

(iv) 11% palmitic acid.

(v) 4% stearic acid.

## 2.2 THE PHYSICOCHEMICAL PROPERTIES OF SOYBEAN OIL ARE GIVEN BELOW

(i) Iodine value

(ii) Peroxide value

(iii) Acid value

### 2.2.1 Iodine Value

The method is based on the treatment of a known weight of oil/fat with a known volume of standard solution of iodine monochloride (ICl). Excess ICl is reacted with KI and the iodine liberated is titrated against $Na_2S_2O_3.5H_2O$ with starch as indicator. The principle of iodine value determination is based on the addition of iodine to the double bonds of unsaturated fatty acids. The result is given in gramm of iodine molecules consumed by 100g of oil sample and is a measure for the unsaturation of oil sample.

### 2.2.2 Peroxide Value

The peroxide number gives information about the number of peroxide compounds in the oil and hence of the age and quality of the vegetable oil. The lower the peroxide numbers the better and/or newer the oil.

### 2.2.3 Acid Value and Free Fatty acids

The acid value corresponds to the amount of carboxylic acid groups in fatty acids and is given in mg KOH per g sample. The older an oil, is the higher the acid value as triglycerides are converted into fatty acids and glycerol upon aging.

## 2.3 DOUBLE BONDS IN VEGETABLE OILS

Among the oils that contain carbon-carbon double bonds as the functional groups,linseed, tung, corn, cottonseed, rapeseed, and soybean are more widely used as polymeric sources. The major constituents of soybean oil are; 53.2% linoleic acid, 23.4% oleic acid, 11 % palmitic acid, 7.8% linolenic acid, and 4% stearic acid. The major constituents of linseed oil are -linolenic acid (60%),linoleic acid (29%), and oleic acid (27%). This composition varies with changes in climatic conditions. On the other hand, tung oil, also called china wood oil, is derived from the seeds or nuts of the trees aleuritesfordii and A. montana. The major constituent of tung oil is eleostearic acid (77–82%), whereas the other important components of tung oil are oleic acid (3.5–12.7%) and linoleic acid (8–10%). It is known that the carbon-carbon double bond in oleic acid is at C9, in linoleic acid it is at C6 and C9, and in linolenic acid it is at C3, C6, and C9., whereas eleostearic acid has double bonds at positions C5, C7, and C9. As shown in the figure 2.2.



Fig. 2.2. Structures showing double Bonds in vegetable oils

Linseed oil and the tung oil are collectively called ‘‘drying oils’’ which are defined as liquid oils that dry in air to form a solid film (these oils have iodine values greater than or equal to 150 units). Soybean oil, sunflower oil, and canola oil are semi-drying oils, with iodine values between 110 units and 150 units. The drying power of such oils is directly related to the chemical reactivity conferred on the triglyceride molecules by the carbon-carbon double bonds of the unsaturated acids, which allows them to react with atmospheric oxygen, thus leading to the process of polymerization to form polymeric networks. Linseed oil, which contains 60% - linolenic acid, is an example of non-conjugated oil, which is rich in polyunsaturated fatty acids. These polyunsaturated fatty acids contain double bonds, which are separated by at least two single bonds. The linolenic acid content in non-conjugated oils plays an important role in the drying process that is generally considered to be the result of a process of autoxidation followed by polymerization when the oil absorbs large amounts of oxygen. The process of autoxidation in the case of non-conjugated oil systems begins with the dehydrogenation of unsaturated fatty acids, such as linolenic acid, by means of atmospheric oxygen. As a result, dehydrogenated radicals are formed and chain polymerization starts with the formation of hydroperoxide. Furthermore, cross-linking takes place to form large molecules**.** Suresh S. Narine and Xiaohua Kong (2005).

2.3.1Mechanism of “Drying Oil” (Auto-Oxidation Of Double Bonds)

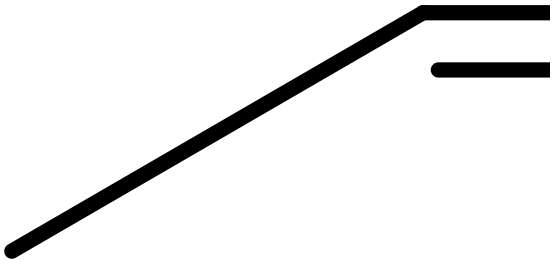


Fig.2.3. Auto-oxidation of double bonds

Tung oil with eleostearic acid as its major component, on the other hand, is an example of conjugated oil systems. The conjugated double bonds of oils, such as those of tung oil, favour polymerisation and oxidation more rapidly than non-conjugated oils. The principal drying component of tung oil is eleostearic acid. As a consequence of this polymerisation, the resultant product obtained is highly resistant to water and alkali.

2.3.2 Processes of Auto-Oxidation include:

i. Induction: This process begins by the autocatalysis of eleostearic acid, and the oxygen uptake starts increasing slowly.

ii. Initiation: Thefilm continues to absorb oxygen from the atmosphere and, as aresult of this absorption, the mass of the film increases and the double bondsof eleostearic acid undergo a rearrangement process. On rearrangement,hydroxyl and hydroperoxyl groups are formed in the film.

iii. Cross-linking: As a result of the above two steps, the number of double bondsdecreases due to cross-linking and, thus, larger molecules are formed.For many applications, tung oils often cure so rapidly that a highly wrinkled surface forms. Therefore, it is necessary to modify the reactivity of tung oil, which is possible by reducing the number of double bonds present. The reactivity can be modified by chemical means, such as the Diels-Alder reaction with a reactive dienophile (Koplan*et al,* 1998) and copolymerization with styrene (Brunner *et al*, 1951 ) and diacrylate(Trumbo *et al,* 2001); this reduces the number of double bonds and causes the cure speed of the copolymers to be slower, resulting in a non-wrinkled surface. Also, by controlling co-monomer stoichiometry, sufficient residual double bonds should remain so that oxidative cure of the copolymers would be still possible.On the other hand, the high degree of unsaturation of this type of drying oil has made it a potential monomer for polymerisation into useful polymers.

More recently, Li and Larock (2001) reported the conversion of tung oil to solid polymers by cationic copolymerization with di-vinylbenzene as a co-monomer. The resulting polymers have proven to be thermosetting materials with good mechanicalproperties and thermal stabilities and may find applications in replacing petroleum-based polymeric materials because of their presumed ability to biodegrade and the low cost of their preparation from renewable natural resources (i.e., vegetable oils).

Furthermore, the multiple double bonds also make tung oil a thermally polymerisable monomer at elevated temperatures. Li and Larock (2003)produced a variety of polymers prepared by thermal copolymerization of tung oil, styrene, and divinyl-benzene in the temperature range of 85–160 $^{O}$C,by varying the stoichiometry, oxygen uptake, peroxides, and metallic catalysts. They found that the stoichiometry and the addition of metallic catalysts greatly affect the mechanical, thermal, and physical properties of the resulting polymers. However, the variations of oxygen uptake and peroxides have little effect.

Li and Larock (2000) also proposed adirect method to convert soybean oil to polymers by cationic copolymerisation with di-vinylbenzene or mixtures of styrene and di-vinylbenzene initiated by boron trifluoride diethyl etherate or other modified initiators. The polymers obtained can range from soft rubbers to hard plastics, depending on the reagents, stoichiometry, and initiators used in the synthetic process. The resulting polymers exhibit thermal, physical, and mechanical properties that were competitive with those of their petroleum-based counterparts, as well as some other very promising properties, including good damping and shape memory properties.Knot et al. (2001) converted soybean oil to several monomers for use in structural applications. They prepared rigid thermosetting resins by using free radical copolymerization of maleates with styrene. The maleates are obtained by glycerol trans-esterification of the soybean

oil, followed by esterification with maleric anhydride.They also synthesized several TAG-based polymers and composites and compared their properties. It was found that the moduli and glass transition temperature ($T_g$) of the polymers varied and depended on the particular monomer and the resin composition. They proposed that the transition from glassy to rubbery behaviour was extremely broad for these polymers as a result of the triacylglycerol (TAG) molecules acting both as cross-linkers as well as plasticizers in the system.

## 2.4EPOXIDATION OF SOYBEAN OIL

### Theory

Epoxidation and hydroxylation are so intimately bound up with the chemistry of peracids (R-$CO_3H$). Peracids are formed by the interaction of carboxylic acids or sometimes their anhydrides, with hydrogen peroxide, usually in the presence of sulphuric acid. It is advantageous to use high-strength hydrogen peroxide (90-95%) to achieve a better result. Large scale manufacture of peracetic acid is based on the atmospheric oxidation of acetaldehyde.

### 2.4.1. Equation of Peracid Formation

$$R\text{-}COOH + H_2O_2 \rightleftharpoons R\text{-}CO_3H + H_2O$$

Peracids are to exist as hydrogen-bonded monomers in solution and as dimers in the crystalline state.

(a) Monomer in solution (b) Dimer in crystalline state

Fig. 2.4: Structures of monomer in solution and dimer in crystalline state

2.5.2 Mechanism of epoxidation

Peracid oxidation is a direct cis addition resulting, possibly from rearrangement within the ∏-complex formed between olefin and peracid. The structures of epoxidation reaction mechanism are given in fig. 2.5

Reaction through the bromohydrin gives the same epoxide as a consequence of *trans* addition followed by *trans* elimination.

Fig.2.5: Structures, showing the mechanism of epoxidation reaction

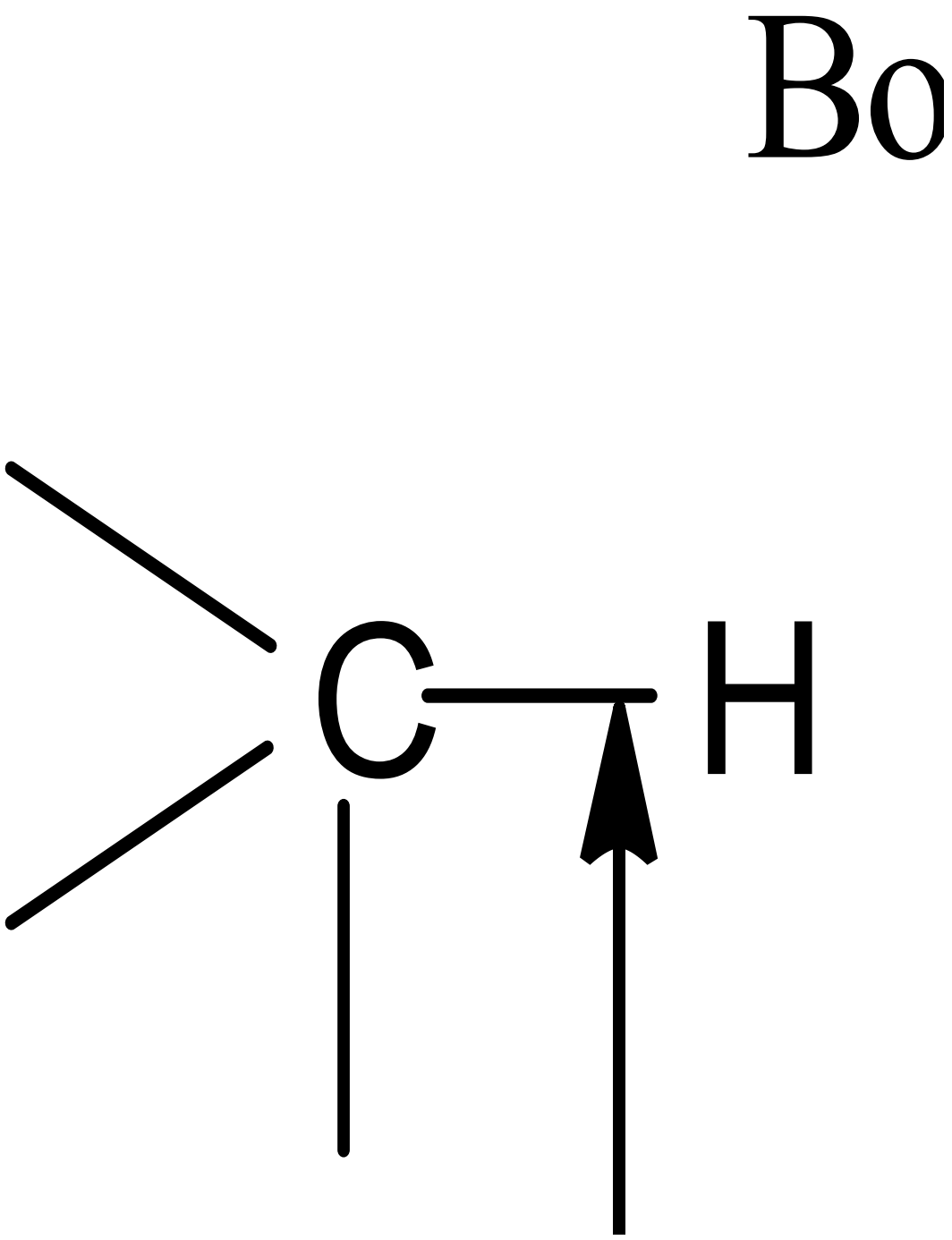
Epoxides are highly active ethers particularly in acid solution where they behave as oxonium-carbonium ion hybrids, undergoing a wide range of reactions.(Gunstone, 1967)

Table2.1FT-IR Characteristic band of epoxylgroups of DGEBA and HDGEBA resins

| Resin | Band ($cm^{-1}$) | Assignment |
|---|---|---|
| DGEBA | » 3500 | O-H stretching |
| | 3057 | C-H stretching of the oxirane ring |
| | 2965-2873 | Stretching C-H of $CH_2$ and CH aromatic and aliphatic |
| | 1608 | Stretching C=C of aromatic rings |
| | 1509 | Stretching C-C of aromatic |
| | 1036 | Stretching C-O-C of ethers |
| | 915 | Stretching C-O of oxirane group |
| | 831 | Stretching C-O-C of oxirane group |
| | 772 | Rocking $CH_2$ |
| HDGEBA | » 3500 | O-H stretching |
| | 3052 | C-H stretching of the oxirane ring |
| | 2937-2862 | Stretching C-H of $CH_2$ and CH |
| | 1448 | Deformation C-H of $CH_2$ and $CH_3$ |
| | 1368 | Deformation $CH_3$ of C-( $CH_3)_2$ |
| | 1098 | Stretching C-O-C of ethers |
| | 909 | Stretching C-O of oxirane group |
| | 846 | Stretching C-O-C of oxirane group |
| | 759 | Rocking $CH_2$ |

(George et al 1991, Mijovic et al 1995)

Table 2.2 IR Table (short summary of common absorption frequencies)




**(www.cpp.edu/...psbeauchamp/pdf/424_spectra_table.pdf)**

# IR Flow

## 2.5VISCOSITY OF POLYMER SOLUTION

Rheology by definition is the science of deformation and flow of matter. Rheological measurements provide useful behavioural and predictive information for various products in addition to knowledge of the effects of processing, formulation changes, and ageing phenomena. Material processability can also be determined through rheological studies. Rheology deals with those properties of materials that determine their response to mechanical force. For solids, this involves elasticity and plasticity. For fluids, on the other hand, rheological studies involve viscosity measurements. Viscosity is a measure of the internal friction of a fluid. For example, it has been observed that even at low concentrations of a dissolved polymer, the viscosity of a solution relative to that of the pure solvent is increased appreciably. This is due to the unusual size and shape of polymer molecules and the nature of their solutions. Thus, measurements of the viscosity of polymer solutions can provide information about monomer molecular weight, molecular weight distribution, and other material characterisation parameters. For every dilute polymer solution, polymer coils are widely separated and do not overlap. At a critical concentration $C^*$, marking the transition from the extremely dilute to dilute regions, the hydrodynamic volumes of individual coils start to touch. As the concentration increases, the coils begin to overlap and finally entanglements are formed that increased the viscosity. The critical concentration ($C^*$) may be marked by abrupt increase in the specific viscosity. In general, the effect of molecular weight and solution viscosity can be modelled as

$$\eta = K(CP)^{\alpha}M^{\beta} \qquad (1)$$

Where K = constant, $\alpha$ and $\beta$ are parameters, $\eta$ = specific viscosity, M= molecular weight of polymer, C= concentration of polymer solution and P= density of the solvent. The ratio $\beta/\alpha$ is

usually in the range from 0.54 to 0.74. The presence of a solvent (plasticizer) has two effects on polymer viscosity in the concentrated solution region

(i) The solvent lowers the $T_g$ of the polymer

(ii) The solvent increases the molecular weight between entanglement as shown below

$$M_e = M_e^0 / Ø \quad (2)$$

where $M_e^0$ is the molecular weight between entanglement for undiluted polymer, Ø = volume fraction of the solvent.

As the polymer concentration increases, polymer solution becomes more non-Newtonian as the number of entanglement increases.

2.5.1 Pressure Flow (Poiseuille).

For a flow through a capillary tube, it is assumed that flow is isothermal, fully developed, incompressible, laminar and steady. The volumetric flow rate Q, through a capillary tube is similar to the Hagen-Poiseuille equation given as

$$Q = \pi R^4 \Delta P / 8\mu L \quad (3)$$

where, Q = volumetric flow rate, R = radius of capillary tube, ΔP = pressure change, L = length of capillary tube from one mark to the other. Similar models can be developed for isothermal pressure flow through other simple flow geometries such as an annulus or infinitely wide plates.

2.5.2 Capillary Rheometry.

The shear stress on a fluid element in the capillary only upon the pressure drop and distance from the centerline is totally independent of whether the fluid is Newtonian or non-Newtonian. (Fried, 2007a)

2.5.3 Capillary Viscometer.

Capillary viscometers may be Ostwald-Fenske or Ubbelohde types. The latter have the advantage that different solution concentration can be directly in the viscometer by successive dilutions with pure solvent. During measurement, the viscometer is immersed in a constant temperature bath controlled to within 0.02 $^0$C of the set temperature typically 25 or 30 $^0$C.

(Fried, 2007b)

2.5.4 Intrinsic Viscosity Measurement.

A method widely used for routine molecular weight determination is based upon the determination of intrinsic viscosity [Ⴖ], of a polymer solution through measurement of polymer solution viscosity. Molecular weight is related to [Ⴖ], by the Mark-Houwink-Sakurah equation given as

$$[Ⴖ], = K\dot{M}_v^a \quad (4)$$

where $\dot{M}_v$, = viscosity average molecular weight, defined for a discrete distribution of molecular weights as;

$$\dot{M}_v = [\Sigma NiMi^{1+a}/ \Sigma N_iM_i]^{1/a} \quad (5)$$

where $N_i$ and $M_i$ are the number of moles and molar mass of the polymer repeat unit. Both K and a are empirical (Mark-Houwink) constants that are specific for a given polymer at definite solvent and temperature. The exponential (a) normally lies between the value of 0.5 for a θ (theta(room temperature)) solvent and 0.1 for a thermodynamically good solvent. Table 2.3 gives Mark-Houwink parameter for some polymers at 25$^O$C.

Table 2.3Mark-Houwink parameters for some polymers at $25^{O}C$

| Polymers | Solvents | K ($10^3$ $mLg^{-1}$) | A |
|---|---|---|---|
| Cellulose acetate | THF | 51.3 | 0.69 |
| Polycarbonate | THF | 38.9 | 0.70 |
| Polydimethylsiloxane(PDMS) | Toluene | 2.4 | 0.84 |
| Poly(2,6-dimethyl-1,4-phenylene oxide) | Toluene | 28.5 | 0.68 |
| (PDPO) | Benzene | 5.5 | 0.76 |
| Poly methyl meta acrylate(PMMA) | THF | 14 | 0.70 |
| Polystyrene (PS) | Benzene | 9.2 | 0.74 |
| Polystyrene (PS) | Toluene | 7.5 | 0.75 |
| Polystyrene (PS) | Butanone | 42.0 | 0.62 |
| Polyvinyl acetate (PVA) | THF | 16.3 | 0.77 |
| Polyvinyl chloride (PVC) | | | |

**(**Fried, 2001c)

Intrinsic viscosity is implicitly expressed by the Huggins equation as

$$\eta_i/C = [\eta] + K_H[\eta]^2C \quad (6)$$

Where $K_H$ is a dimensionless parameter (the Huggins coefficient), whose value depends upon temperature as well as the specific polymer/solvent combination. The parameter $\eta_i$ is called the relative viscosity increment, which is defined as;

$$\eta_i = (\eta - \eta_s)/\eta_s \quad (7)$$

Where $\eta$ and $\eta_s$ are the viscosities of the dilute polymer solution and the pure solvent respectively. The ratio $\eta_i/C$ is commonly called the reduced viscosity $\eta_{red}$ or viscosity number according to recommended IUPAC nomenclature. As indicated in the Huggins equation (6), $[\eta]$ can be obtained from the intercept of a plot $\eta_{red}$vs concentration. In actual practice, $\eta_{red}$ is obtained at different concentration, not by direct measurement of solution and solvent viscosity, but by measurement of time required for a dilute solution (T) and pure solvent ($T_s$) to fall from one fiducial mark to another in a small glass capillary. If these efflux times are sufficiently long (e.g> 100 seconds), the relative viscosity increment can be obtained as

$$\eta_i = T\text{-}T_s / T_s \qquad (8)$$

In addition to determination of molecular weight, measurement of intrinsic viscosity can also be used to estimate chain dimension in solution. The mean-square end to-end distance ($r^2$) is related to intrinsic viscosity by

$$(r^2) = ( M[\eta]/Ø )^{2/3} \qquad (9)$$

Where Ø is considered as the universal constant (Ø = 2.1±0.2 x $10^{21}$dLmol$^{-1}$cm$^{-3}$) known as Flory constant.

## 2.6 THERMODYNAMICS OF POLYMER SOLUTION

The behavior of polymer solutions toward solvent is characteristically different from that of low molecular weight substance. The size and conformation of dissolved polymer molecules require special theoretical treatment to explain their solution properties. Conversely, it is possible to obtain information about the size and shape of polymer molecules from studies of their solution properties. Generally, the solubility of a solute in a solvent is governed by Gibb's free energy given by;

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (10)$$

For an ideal solution in which the molecules of components A and B have roughly the same size, shape and similar force field, (there is no change in the enthalpy of mixing, therefore, $\Delta H_m = 0$, then $\Delta G_m = 0$) Raoult's law is obeyed. This law states that "the partial vapour pressure of each component in the mixture is proportional to its mole fraction".

$$P_A = P_A^o (N_A/N_A + N_B) = P_A^o n_A \quad (11)$$

Where $n_A$, $P_A$ and $P_A^o$, are the mole fraction, vapour pressure of solvent and pure solvent respectively. These partial vapour pressures are related to solvent activity ($\alpha$) by

$$\alpha = P_A/P_A^0 \quad (12)$$

For an Ideal solution, $n_A \equiv \alpha_A$.

Thus, the activity ($\alpha$) of a solvent is related to its chemical potential ($U_A$) by

$$\text{In } \alpha = \Delta U_A/KT \quad (13)$$

Thus, the partial molar Gibb's free energy of mixing ($\Delta \bar{G}_M$)is related to the chemical potential ($\Delta U$) by

$$\Delta U_i = U_i - U_i^0 = \Delta \bar{G}_M = (d\Delta G_M/dn_i)_{T,P} \quad (14)$$

Thus, $\text{In } \alpha = \Delta \bar{G}_A / KT$ or

$$\Delta G_A = KT \text{In} \alpha_A \quad (15)$$

On substituting equation (12) into equation (15), $\Delta G_A$becomes

$$\Delta G_A = KT \text{ In } (P_A/P_A^0) = KT \text{ In } n_A \quad (16)$$

Hence, the total Gibb's free energy of mixing $\Delta G_M$ is given by

$$\Delta G_M = N_A \Delta G_A + N_B \Delta G_B = KT ( N_A \text{ In } n_A + N_B \text{ In } n_B ).$$

Since $\Delta H = 0$, Then, on substituting in equation (10) gives the entropy of mixing $\Delta S_m$ as

$\Delta G_m = -T\Delta S_m$, Thus,

$$\Delta S_m = -K( N_A \text{ In } n_A + N_B \text{ In } n_B ) \quad (17)$$

This is positive for all ideal compositions, so that, by the second law (i.e second derivative of equation (17)) , spontaneous mixing occurs in all proportions.

However, polymer solutions invariably exhibit large deviation from Raoul's law except at extreme dilutions where ideal behaviour is approached as an asymptotic limit.

Thus, for a polymer solution (i.e where $\Delta H \neq 0$), the entropy of mixing ($\Delta S_m$) of a low molecular weight solvent with a high molecular weight polymer is smaller than that of an ideal solution given in equation (17). This is due to loss in conformational entropy which resulted from the linkages of individual repeat unit along a polymer chain.

Therefore,

$$\Delta S_m = - K (n_1 In\phi_1 + n_2 In\phi_2) \quad (18)$$

Where, $Ø_1$ and $Ø_2$ are the lattice volume fractions of component 1(solvent or solute), and 2 (polymer) respectively given by;

$$\phi_1 = n_1/(n_1 + rn_2) , \ \phi_2 = n_2/(n_2 + rn_1).$$

Where, r is a segment of the polymer chain which is equivalent to size of solvent molecule given as

$r = V_2/V_1$ (ratio of polymer volume to solvent volume).

Therefore, since $\Delta H \neq 0$, then $\Delta H$ is given by

$$\Delta H_m = KT\chi_{12} n_1\phi_2 \quad (19)$$

where, $\chi_{12}$ is called Flory-Huggins interaction parameter. Thus, combining equation (18) and (19) gives the well- known Flory-Huggins expression for the Gibb's free energy of mixing $\Delta G_m$ as

$$\Delta G_m = KT(n_1 In\phi_1 + n_2 In\phi_2 + \chi_{12} n_1\phi_2)$$

(20)(Billmeyer, 2005)

### 2.6.1 Criteria for Polymer Solubility

The Solution Process.

Dissolving a polymer is a slow process that occurs in two stages.

Firstly, solvent molecules slowly diffuse into the polymer to produce a swollen gel. (This may be all that happens, if for example, the polymer-polymer intermolecular forces are high because of crosslinking, crystallinity or strong hydrogen bonding). But, if these forces can be overcome by introduction of strong polymer-solvent interaction then, second stage of solution can take place. In this second stage, the gel will gradually disintegrate into a true solution. Only this second stage can be materially speeded by agitation. Even so, the solution process can be quite slow (days or weeks) for materials of very high molecular weight. (Ebewele, 2000a)

### 2.6.2 Solubility Parameter

Solubility occurs when the free energy of mixing is negative (i.e$\Delta G_m$ = -ve) since $\Delta S_m$ is always positive, the sign of $\Delta G_m$ is defined by the sign and magnitude of $\Delta H_m$ . Thus, for non-polar molecules and in the absence of hydrogen bonding, $\Delta H_m$ is positive. Thus,

$$\Delta H_m = V_1 V_2 (\delta_1 - \delta_2)^2 \qquad (21)$$

Where $V_1$ and $V_2$ refer to volume fraction of solvent and polymer respectively, $\delta$ = solubility parameter.

The value of the solubility parameter approach is that $\delta$ can be calculated for both polymer and solvent. As a first approximation, and in the absence of a strong interaction such as hydrogen bonding, solubility can be expected if the $\delta_1 - \delta_2$ is less than 3.5 - 4.0, but not if it is appreciably

larger. The easiest way to determine $\delta_2$ for a polymer of known structure is by use of the molar attraction constant (E) given as

$$\delta_2 = \rho\Sigma E/M \quad (22)$$

where ρ and M are the density and molecular weight of the polymer repeat unit respectively.

The solubility parameter (δ) is also related to cohesive energy density (CED) or molar energy of vaporization of a pure liquid ($\Delta E^v$) as

$$\square = \sqrt{CED} = \sqrt{\Delta E^v/V} \quad (23)$$

where V = molar volume of the liquid.

Given the value of δ for both solvent and polymer, the enthalpy of mixing can be estimated from the Scatchard-Hildebrand equation as

$$\Delta H_m = V(\square_1 - \square_2)^2 \Phi_1 \Phi_2 \quad (24)$$

where V = volume of the mixture.

Thus, the interaction parameter ($\square_{12}$) can be estimated from this value of $\Delta H_m$ as

$$\square_{12} = (v_1(\square_1 - \square_2)^2)/RT \quad (25)$$

Table 2.4.Solubility Parameter of Some Common Solvents and Polymers

| Solvents | Solubility parameter ( ) | |
|---|---|---|
| | $(MPa)^{1/2}$ | $(Calcm^{-3})^{1/2}$ |
| n-Hexane | 14.9 | 7.28 |
| Carbon tetrachloride | 17.8 | 8.70 |
| Toluene | 18.2 | 8.9 |
| Benzene | 18.6 | 9.09 |
| Chloroform | 19.0 | 9.29 |
| Tetrahydrofuran(THF) | 19.4 | 9.48 |
| Chlorobenzene | 19.6 | 9.58 |
| Methylchloride | 20.3 | 9.92 |
| 1,4-Dioxane | 20.5 | 10.0 |
| n-Methyl-2 pyrodine | 22.9 | 11.2 |
| Di-methyl formamide | 24.8 | 12.1 |
| Methanol | 29.7 | 14.5 |
| Acetone | 19.9 | 9.78 |
| Water | 47.9 | 23.4 |
| Styrene | 19.0 | 9.29 |
| Polymers | | |

| | | |
|---|---|---|
| Poly(isobutylene) | 15.5 | 7.58 |
| Polysulfone | 20.3 | 9.92 |
| Poly(vinylchloride) | 21.5 | 10.5 |
| Polystyrene | 22.5 | 11.0 |
| Polymetamethylcrylate(PMMA) | 22.7 | 11.7 |
| Cellulose acetate | 25.1 | 12.3 |
| Polyacrylonitrile | 25.3 | 12.4 |
| Polyvinyl acetate | 25.7 | 12.7 |
| Polypropylene | 16.6 | 8.1 |
| Polyethylene | 16.2 | 7.9 |
| Polyethyleneteraphthalate (PET) | 21.9 | 10.7 |
| Poly butadiene | 17.6 | 8.6 |
| Polytetrafluoroethylene (PTFE) | 12.7 | 6.2 |

(Fried, 2007c)

## 2.7 ALLOYS AND BLENDS

The traditional method of enhancing properties by adding fillers and reinforcements, while still effective in some applications, has been inadequate for coping with the increasing performance requirements of design problems and the changing material specifications. Development of new resin systems to meet demands for high performance materials would undoubtedly take too long and would certainly be too expensive since it would require huge investments in totally unexplored technologies and new plant facilities. An alternative to the development of new

polymers is the development of alloys and blends that are a physical combination of two or more polymers to form a new material. The basic objective is to combine the best properties of each component in a single functional material that consequently has properties beyond those available with the individual resin components and that is tailored to meet specific requirements. Another goal is to optimize cost/performance index and improve processability of a high temperature or heat-sensitive polymer. Although the terms alloys and blends are used interchangeably, they differ in the levels of inherent thermodynamic compatibilities and in resulting properties. In general, a necessary though not sufficient condition for thermodynamic compatibility (miscibility), is a negative change in the free energy of mixing, $\Delta G_m$, given in equation (10).

Generally, because of their large size and unfavourable energy requirements, chains from a given polymer prefer to intertwine among themselves than with those of another polymer. Consequently, the magnitude of $\Delta S_m$ is usually small. Therefore, for two polymers to be thermodynamically miscible, $\Delta H_m$ must be negative, zero, or, at most, slightly positive. If $\Delta H_m$ is strongly positive, the components of a physical mixture separate into different phases resulting in a blend. However, some polymers tend to be mutually soluble, at least over a limited concentration range. Such are called alloys. In other words, alloys represent the high end of the compatibility spectrum. Individual polymeric components in alloys are intimately mixed, on a molecular level, through specific interactions such as donor–acceptor or hydrogen bonding between the polymer chains of the different components.

The composition dependence of a given property, P, of a two-component polymer system may be described by

$$P = P_1C_1 + P_2C_2 + IP_1P_2$$

where $P_1$ and $P_2$ are the values of the property for the isolated components and $C_1$, $C_2$ are, respectively, the concentrations of the components of the system. I is the interaction parameter that measures the magnitude of synergism resulting from combining the two components. If I, is positive, then the magnitude of the property for the system exceeds that expected for a simple arithmetic averaging of the two component properties. The system in this case is referred to as synergistic. If I is negative, then the mixture has a property value less than that predicted from the weighted arithmetic average. This is known as non-synergistic. Polymer systems for which I is either zero or nearly zero are called additive blends.

The fig. 2.6 shows illustration indicating composition dependence of two component polymer system

Fig. 2.6 Composition dependence of the property of a two-component polymer system

They have properties that are essentially arithmetic averages of the properties of their components. Compatible polymer blends form single-phase systems and have a single property,

like the glass transition temperature, the value of which is generally the weighted arithmetic average of the values of the components of the blend. At certain compositions, some compatible polymer blends exhibit strong intermolecular attraction and hence have a high level of thermodynamic compatibility. This results in properties superior to those of the individual components alone. Such blends display synergistic properties (e.g., tensile strength and modulus). Only a few commercially available polymers are truly compatible. Examples of the most significant commercial engineering alloys are polystyrene (PS)-modified poly(phenylene oxide) (PPO) and polystyrene (PS)-modified poly(phenylene ether) (PPE). Incompatible polymer blends consist of a heterogeneous mixture of components and exhibit discrete polymer phases and multiple glass transition temperatures corresponding to each of the components of the blend. A polymer blend with completely incompatible components has limited material utility because the components separate during processing due to lack of interfacial adhesion, which is required for optimum and reproducible polyblend properties. Improvement in adhesion in such blends can be effected by the addition of compatibilizers. Compatibilizing agents provide permanent miscibility or compatibility between otherwise immiscible or partially immiscible polymers creating homogeneous materials that do not separate into their component parts. The most effective compatibilizing agents are generally block and graft copolymers whose polymer blocks or segments are the same as the components of the polyblend. The inherent compatibility between the segments of the compatibilizer and each component of the blend effectively ties the discrete polymer phases together. It is useful to visualize the function of a compatibilizing agent as akin to that of the emulsifier in water–oil emulsified systems. The primary objectives in blending are to enhance material processing characteristics and optimize product performance while minimizing costs. A common strategy for achieving these objectives is to combine a

crystalline polymer with an amorphous polymer. The aim is to exploit the strengths of each component while deemphasizing their weaknesses. Crystalline materials such as nylon, poly(butylene terephthalate) (PBT), and poly(ethylene terephthalate) (PET) offer excellent chemical resistance, processing ease, and stiffness, but suffer from poor impact strength and limited dimensional stability. On the other hand, amorphous polymers such as polycarbonate (PC) and polysulfone have outstanding impact strength and dimensional stability but poor chemical resistance. Polycarbonate–poly(ethylene terephthalate) blends combine the desirable properties of polycarbonates with the excellent chemical resistance of PET and have been specified for use in many applications, for instance, as replacements for metal, including automotive, lawn and garden appliances and electrical/electronic, consumer, industrial/mechanical, sporting and recreation, and military equipment. A blend of PPO and nylon is used for fenders and rocker panels of some automobiles, applications demanding chemical-resistant performance under high impact and high heat.

(Ebewele, 2000b)

## 2.8 MECHANICAL PROPERTIES OF POLYMERS.

The unique properties of polymers coupled with their light weight make them preferable alternative to metallic and ceramic materials in many applications. In the selection of a polymer for a specific end-use, careful consideration must be given to its mechanical properties. The mechanical behaviour of a polymer is a function of its microstructure or morphology. Polymer morphology itself depends on many structural and environmental factors. Compared to those of metals and ceramics, polymer properties show a much stronger dependence on time and

temperature. This strong time-temperature dependence of polymers is as a result of visco-elastic nature of polymers (Ebewele, 2000c).

### 2.8.1 Mechanical tests

Polymer components, like other materials, may fail to perform their intended functions in specific applications as a result of

(i) Excessive elastic deformation

(ii) Yielding or excessive plastic deformation

(iii) Fracture

Polymers show excessive elastic deformation, particularly in structural, load-bearing applications, due to inadequate rigidity or stiffness. For such failure, the controlling material mechanical property is the elastic modulus. However, the elastic moduli of some polymers are subject to some measure of control through appropriate structural modification. The failure of polymers in certain applications to carry design loads or occasional accidental overloads may be due to excessive plastic deformation resulting from the inadequate strength property of the polymer. For such failure, the controlling mechanical property of primary interest is the yield strength and the corresponding strain. A variety of test methods exist for predicting mechanical performance limits under a variety of loading conditions. These test methods include

(i) Simple tension

(ii) Simple compression

(iii) Shear test-designed to test complex stress states and polymer time-temperature response.

These test methods can be conducted in the various experiments

(a) Stress-strain experiments.

(b) Creep experiments

(c) Stress relaxation experiments

(d) Dynamic mechanical experiments

(e) Impact experiments

### 2.8.2 Stress-Strain Experiments

These experiments have been the most widely used mechanical test but probably the least understood in terms of interpretation. In stress-strain tests, the specimen is deformed (pulled) at a constant rate, and the stress required for this deformation is measured simultaneously. The utility of stress-strain tests for design with polymeric materials can be greatly enhanced, if the tests are carried out over a wide range of temperature and strain rate.

### 2.8.3 Creep Experiments

In creep tests, a specimen is subjected to a constant load, and strain is measured as a function of time. The test specimen in a laboratory setup can be a film or bar clamped at one end to a rigid support, while the load is applied suddenly at the other end. The elongation may be measured at time interval using a cathetometer or a travelling microscope. Measurement may be conducted in an environmental chamber. Creep tests are made mostly in tension, but creep experiments can

also be done in shear, torsion, flexure, or compression. Creep data provide important information for selecting a polymer that must sustain dead loads for long periods. Here, the parameter of interest to the engineer is the compliance (J), which is a time-dependent reciprocal of modulus. It is the ratio of time-dependent strain to the applied constant stress.

$$J(t) = \square (t) / \sigma_0 \qquad (26)$$

2.8.4 Stress Relaxation Experiments

In stress relaxation experiments, the specimen is rapidly (ideally, instantaneously) extended a given amount, and the stress required to maintain this constant strain is measured as a function of time. The stress that is required to maintain the constant strain decays with time. When this stress is divided by the constant strain($\square$ ), the resultant ratio is the relaxation modulus donated as $E_r(t,T)$ which is a function of time and temperature. Stress relaxation data provide useful information about the visco-elastic nature of polymers.

2.8.5 Dynamic Mechanical Experiments

In dynamic mechanical tests, the response of a material to periodic stress is measured. There are many types of dynamic mechanical test instruments. Each has a limited frequency range, but can cover frequency from $10^{-5}$ to $10^{6}$ cycles per second. The most popular is the torsion pendulum. In this instrument, a polymer is clamped at one end, and the other end is attached to a disk that is free to oscillate. As a result of the damping characteristics of the test sample, the amplitude of the oscillation decays with time. This can be illustrated by considering the response of elastic and viscous materials to imposed sinusoidal strain ($\square$) as

$\square = \square_0 \sin(\omega t)$

(27)

Where $\square_0$ is the amplitude and $\omega$ is the frequency (in radian per second, $\omega = 2\pi f$; f is in cycle per second). For a purely elastic body, Hook's law is obeyed. Consequently,

$$\sigma = G\ \square_0 \sin(\omega t) \qquad (28)$$

where G is the shear modulus. From both equations for elastic body, both stress and strain are in phase. For a purely viscous fluid. Newton's law is obeyed. Consequently,

$$\sigma = \eta d\square$$

i.e $$\sigma = \eta\ \square_0 \omega \cos(\omega t) \qquad (29)$$

In this case, the shear stress and strain are $90^0$ out of phase. Thus, the response of viscoelastic materials fall within these two extremes. It follows that the sinusoidal stress and strain for viscoelastic materials are out of phase by an angle, say $\delta$ defined as the lag angle between the stress and strain given by

$$\tan\delta = G''/G' \qquad (30)$$

where G' is the real part of the complex modulus ($G'' = G' + iG''$), and G'' is the imaginary part of the modulus. In physical terms, $\tan\delta$ donates the damping characteristics of the material. It is a measure of the ratio of the energy dissipated as heat to the maximum energy stored in the material during one cycle of oscillation.

A convenient measure of damping is in terms of quantities determined from the experiment. Thus;

$$\tan\delta = (1/\pi)\ln(A_1/A_2) \quad (31)$$

Where $A_1$, and $A_2$ are the amplitudes of two consecutive peaks. Alternately, this may be expressed in terms of log decrement ($\Delta$) for free vibration instruments like the torsional pendulum.

$$\Delta = \ln(A_1/A_2) = (A_2/A_3) = (1/n)\ln(A_i/A_{i+n}) \quad (32)$$

It follows from equations (31) and (32) that

$$\Delta = \pi\tan\delta \quad (33)$$

Data from the dynamic mechanical measurement can provide direct information about the visco-elastic response of a polymer. It is a versatile tool for studying the effects of molecular structure on polymer properties. It is a sensitive test for studying glass transition temperature and secondary transitions in polymer and the morphology of crystalline polymers

2.8.6 Impact Experiments

Polymers may also fail in service due to the effects of rapid stress loading (impact loads). Various test methods have been proposed for assessing the ability of a polymeric material to withstand impact loads. These include measurement of area under the stress-strain curve in the high-speed (rapid) tensile test, the measurement of the energy required to break a specimen by a ball of known weight released from a predetermined height, the so-called falling ball or dark test, and the Izod and Charpy tests. The most popular of these test methods are the Izod and Charpy

impact strength tests. Essentially, the Izod test involves the measurement of energy required to break a notched cantilever specimen that is clamped rigidly at one end and then struck at the other end by a pendulum weight. In the case of the Charpy test, a hammer-like weight strikes a notched specimen that is rigidly held at both ends. The energy required to break the specimen is obtained from the loss in kinetic energy of the hammer. Another test that is emerging as a substitute for the impact test is the measurement of fracture toughness, which in essence measures the resistance to failure of a material with a predetermined crack.

Impact tests provide useful information in the selection of a polymer for a specific application, such as determining the suitability of a given plastic as a substitute for glass bottle or a replacement for window glass (Ebewele, 2000d). The table 2.5 shows the impact energies of some polymers.

Table 2.5 Impact energies of some polymers

| Polymer | Grade | Impact energy (J) |
|---|---|---|
| Polystyrene | General purpose | 0.34-0.54 |
| Polystyrene | High Impact | 0.68-10.80 |
| PVC | Rapid | 0.54-4.07 |
| PVC | Plasticized | 1.36-20.33 |
| Polypropylene | Unmodified | 0.68-2.71 |
| PMMA | Molding | 0.41-0.68 |
| PMMA | High impact | 1.90 |
| Poly (oxy-methylene) | | 1.90-3.12 |
| Nylon 6,6 | | 1.36-3.39 |
| Nylon 6 | | 1.36-4.07 |
| Poly(propyleneoxide) | | 6.78 |
| Polycarbonate | | 16.26-24.39 |
| Polyethylene | Low density | 21.70 |
| Polyethylene | High density | 0.68-27.10 |
| Poly (tetra-fluoroethylene) | | 4.07 |
| Polypropylene | | 0.68-2.71 |

(Ebewele, 2000e)

Generally, from the table, it can be seen that brittle polymers like general-purpose polystyrene have low impact resistance, while most engineering thermoplastics like polyamides, polycarbonate, and poly (oxy-methylene) and some commodity thermoplastics like polyethylene, polypropylene and poly (tetra-fluoroethylene) have high impact strength.

2.8.7 Stress-Strain Behaviour of Polymers

In stress-strain experiments, a polymer sample is pulled (deformed) at a constant elongation rate, and stress is measured as a function of time. (ASTM D638M).

Generally, the polymer specimen, which may be rectangular or circular in cross-section, is molded or cut in the form of a dog bone. It is clamped at both ends and pulled at both ends and pulled at one of the clamped ends (usually downward) at constant elongation. The shape of the test specimen is designed to encourage failure at the thinner middle portion. The central section between clamps is called the initial gauge length, $L_0$. The load or stress is measured at the fixed end by means of a load transducer as a function of the elongation, which is measured by means of mechanical, optical, or electronic strain gauges. The experimental data are generally stated as engineering (nominal) stress ($\sigma$) vs engineering (nominal) strain ( ). The engineering stress is defined as

$$\sigma = F/A_0 \qquad (34)$$

Where F = the applied load, $A_0$ = original cross-sectional area over the specimen.

The engineering strain is given by

$$\varepsilon = (L - L_0) / L_0 = \Delta L / L_0 \quad (35)$$

where $L_0$ = original length, $\Delta L$ = elongation or change in the gauge length,

L = instantaneous gauge length.

Engineering stress and strain are easy to calculate and used widely in engineering practice. However, engineering stress-strain curves generally depend on the shape of the specimen. A more accurate measure of intrinsic material performance is plots of true stress vs true strain, (Ebewele, 2000f).

### 2.8.8 Deformation of Solid Polymers

To relieve stress, all materials under the influence of external load undergo some deformation. In some cases, this deformation may be quite large and perceptible, like the boughs of a mango tree under the weight of its fruit. In some other cases, deformation may be imperceptibly small, for example, a fly perching uninvitedly, on the dinning table. Irrespective of our ability to observe it, some deformation always occurs when stresses are imposed on a material. Solid polymers undergo either elastic deformation or plastic deformation or combination of both at some certain stress conditions. Plastic deformation involved a permanent set when the applied load is removed. For most materials, Hook's law is obeyed within the elastic limit,i.e stress is proportional to strain. However, proportionality between the stress and strain does not always hold when a material exhibit elastic behaviour. A typical example is rubber, which is elastic but does not show Hookean behaviour over the entire elastic region.

The data on mechanical properties that are obtainable from stress-strain experiments are as follows;

Stiffness – defined as the ability to carry stress without changing dimension. The magnitude of Modulus of elasticity is a measure of this property or ability

Elasticity – defined as the ability to undergo a reversible deformation or carry load without suffering a permanent deformation. It is indicated by the elastic limit or from a practical point of view, the proportional limit or yield point.

Resilience – defined as the ability to absorbed energy without suffering permanent deformation. The area under the elastic portion of the stress-strain curve gives the resilience energy.

Strength – defined as the ability to sustain dead load. It is represented by the tensile strength or the stress at which the specimen rupture.

Toughness – defined as the ability to absorbed energy and undergoes extensive plastic deformation without rupturing. It is measured by the area under the stress-strain curve.

The response of material to applied stress may be described as ductile or brittle depending on the extent to which the material undergoes plastic deformation before fracture. Ductile materials posses the ability to undergo plastic deformation whereas, Brittle materials fail (rupture) with little or no plastic deformation(Ebewele, 2000g). The table 2.6 shows the mechanicalproperties of some selected polymers, whereas table 2.7 shows the characteristic features of polymer stress-strain behaviour.

Table 2.6 Mechanical properties of selected polymers

| Polymers | Passion ratio | Elastic modulus ($10^3$ psi) | Yield strength ($10^3$ psi) | Ultimate strength ($10^3$psi) | Elongation to fracture(%) |
|---|---|---|---|---|---|
| Polypropylene | 0.32 | 1.5 – 2.25 | 3.4 | 3.5 – 5.5 | 200 – 600 |
| Polystyrene | 0.33 | 4 – 5 | - | 5.5 – 8 | 1 – 2.5 |
| PMMA | 0.33 | 3.5 – 5 | 7 – 9 | 7 – 10 | 2 – 10 |
| LDPolyethylene | 0.38 | 0.2 – 0.4 | 1 – 2 | 1.5 – 2.5 | 400 – 700 |
| Polycarbonate | 0.37 | 3.5 | 8 – 10 | 8 – 10 | 60 – 120 |
| Rigid PVC | 0.40 | 3 – 6 | 8 – 10 | 6 – 11 | 5 – 60 |
| PTFE | 0.45 | 0.6 | 1.5 – 2 | 2 – 4 | 100 – 350 |

Table 2.7 Characteristic features of polymer stress-strain behaviour.

| Material stress-strain behavior | Elastic modulus | Yield point | Tensile strength | Elongation at break |
|---|---|---|---|---|
| Soft and weak (polymer gels) | Low | Low | Low | Moderate |
| Hard and brittle (PS) | High | Practically non-existent | High | Low |
| Hard and strong (PVC) | High | High | High | Moderate |
| Soft and tough (rubbers and plasticized PVC) | Low | Low | Moderate | High |
| Hard and tough (cellulose acetate, nylon) | High | High | High | High |

(Ebewele, 2000h)

## 2.9EFFECTS OF STRUCTURAL AND ENVIRONMENTAL FACTORS ON MECHANICAL PROPERTIES

The factors include;

a. Molecular weight
b. Cross-linking
c. Crystallinity
d. Copolymerization
e. Plasticizers
f. Polarity
g. Steric factor
h. Temperature
i. Strain rate
j. Pressure

### 2.9.1Effect of Molecular Weight on Mechanical Properties

Generally, molecular weight has no practically effect on the modulus in the glassy region (below $T_g$). The drop in modulus and the location of the $T_g$ are also almost independent of the molecular weight since $T_g$ represent the onset of cooperative motion of the chain segment. It is therefore expected that the number of chain entanglements (which increases with increasing molecular weight) will hardly affect such segmental mobility, and consequently $T_g$ is independent of molecular weight. In contrast to the $T_g$, $T_{fl}$ (rubber to – melt – flow transition temperature) is strongly dependent on the molecular weight. Movement of entire molecule is associated with viscous flow. This obviously will depend on the number of entanglements. The higher the

molecular weight, the higher must be the temperature at which viscous flow becomes predominant over rubbery behavior. Consequently, for high molecular weight polymers, $T_{fl}$ is high and rubbery plateau long, whereas, for low molecular weight polymers, the rubbery plateau is absent or very short.

### 2.9.2 Effect of Cross-Linking on the Mechanical Properties

Cross-linking involves chemically connecting polymer molecules by primary valence bonds. This imposes obvious restrictions on molecular mobility. Consequently, relative to uncross-linked polymers, cross-linking increases polymer ability to resist deformation under load, i.e increases its modulus in the rubbery region. The effect of cross-linking on modulus increase in the glassy region is relatively small. However, as the cross-linked density is increased, the restriction on molecular mobility becomes substantial and much higher energy will be required to induce segmental motion ($T_g$ increases).

### 2.9.3Effect of Crystallinity on the Mechanical Properties

Crystallinity in a polymer is the result of ordered molecular aggregation, with molecules held together by secondary valance bonds. Therefore, crystallinity may be viewed as a form of physical cross-linking which is thermo-reversible. Crystallinity has small effect on the modulus below the $T_g$, but has a pronounce effect above the $T_g$. There is a drop in modulus at the $T_g$, the intensity of which decreases with increasing degree of crystallinity (i.e increasing the crystallinity increases the modulus). Since the crystallites have much higher moduli than the amorphous segments, crystallites can be regarded as the rigid fillers in an amorphous matrix.

2.9.4Effect of Copolymerization

In copolymers, strength properties are dedicated by the dispersed phase. For example, in styrene // butadiene // styrene block copolymer of which the butadiene is the dispersed phase has a higher tensile strength than butadiene // styrene // butadiene block copolymer in which styrene is the dispersed phase. Copolymers are two types;

i. Random and alternating copolymers which are homogeneous with single $T_g$ that is intermediate between those of two homopolymers.
ii. Block and graft copolymers which exhibit phase separation with two distinct $T_g$ one for each homopolymer.

It is important to note that copolymerisation essentially shift the modulus-temperature curve the same way as $T_g$ . In copolymerization, the molecules are interconnected by physical cross-links due to secondary forces which are also thermo-reversible.

2.9.5Effect of Plasticizers

Plasticizers are low-molecular weight, usually high boiling liquids that are capable of enhancing the flow characteristics of polymers by lowering their glass transition temperatures. Modulus, yield, and tensile strengths generally decrease with the addition of plasticizers to a polymer. Generally, on plasticization, a solid polymer undergoes a change from (hard and brittle), to (hard and tough), and to (soft and tough).

2.9.6Effect of Polarity

The $T_g$ of the polar PVC is about 90 $^{O}$C higher than that of the nonpolar polypropylene. As the methyl group and chlorine atom occupy about the same volume, the differences in mechanical

behaviour can only be due to the relative polarities of the two polymers. However, the effect of substitution of the chlorine atom for the methyl group depends on the molecular environment of the chlorine atom. The further the chlorine atom is from the main chain, the smaller its effect on the $T_g$. Also, polarity increases the modulus especially in the glassy region.

2.9.7Steric factors

In discussing the influence of steric features on mechanical properties, it is convenient to consider the side chains and main chain separately. The effects of flexible side chain differ completely from those of stiff side chains. Long, flexible side chains reduce the $T_g$ while stiff side chain increases $T_g$. long, flexible side chain increases the free volume and ease the steric hindrance from neighbouring chains and as such facilitate the movement of the main chain. Branched side chains, particularly if the branched point is located close to the main chain, increases the $T_g$. Structural changes, even if minor near or within the main chain can produce drastic effects on the mechanical properties. In general, the introduction of ring system into the main chain can provide a better structural mechanism for toughening polymers than chain stiffening by bulky side group. For example, polycarbonate, polysulfone, and polyphenylene oxide, all have high impact strength, whereas poly-(vinylcarbozole) with comparable $T_g$ is brittle.

2.9.8Effect of Temperature

The mechanical properties of polymers are generally more susceptible to temperature changes than those of metals and ceramics. In general, the modulus of polymer decreases with increasing temperature. However, the rate of decrease is not uniform. The drop in modulus is more pronounced at temperature associated with molecular transitions. As the temperature is increased

to a level that can induce some form of molecular motion, a relaxation process ensues and there is a drop in modulus. At the temperature below $T_g$, the polymer is rigid and glassy, in the region, there are usually one or more secondary transitions that are related either to movements of side chains or to restricted movements of small parts of the main chain. For secondary transitions, the drop in modulus is about 10 – 50%, while primary transitions like $T_g$ and $T_m$ which involve large-scale main chain motion, the drop in modulus varies from one to three orders of magnitude depending on the type of polymer. If no molecular relaxation process occurs over a particular temperature range, the modulus decreases rather slowly with increasing temperature. In this case, the decrease in modulus is due to the normal reduction in intermolecular forces that occurs with an increase in temperature.

### 2.9.9Effect of Strain Rate

Polymers are very sensitive to the strain rate of testing. As the strain rate is increased, polymers in general show a decrease in ductility, while the modulus and the yield or tensile strength increases. The sensitivity of polymers to strain rate depends on the type of polymer: for brittle polymers the effect is relatively small, whereas, for rigid, ductile polymers and elastomers, the effects can be quite substantial if the strain rate covers several decades.

Polymers show a similar response to temperature and strain rate(time), as might be expected from the time-temperature superposition principle. Specifically, the effect of decreasing temperature is equivalent to that of increasing strain rate. Materials deform to relieve imposed stress. High strain rates preclude such deformation and therefore result in brittle failure.

### 2.9.10Effect of Pressure

The imposition of hydrostatic pressure on a polymer has a tremendous effect on its mechanical properties. The modulus and yield stress increase with increasing pressure. This behaviour is general for all polymers. However, the effect of pressure on tensile strength and elongation-at – break increases for some ductile polymers, but decreases for most brittle polymers and polymers such as PE, PTFE and PP, which exhibit cold drawing at normal pressure. In some brittle polymers like PS, brittle – ductile transition is induced beyond a certain critical pressure.

The increase in modulus and yield stress with increase in pressure is to be expected on the basis of the available free volume. An increase in pressure decreases the free volume (i.e increase the packing density) and as such enhances the resistance to deformation (modulus) or delays the onset of chain slippage or plastic deformation (yielding). The embrittlement of polymers capable of cold drawing with increase in pressure can be rationalized on the basis of the reduction in chain mobility associated with the decrease in free volume. Also, with an increase in pressure, the occurrence of relaxation processes responsible for cold drawing phenomenon is delayed to higher temperature. In other words, subjecting a polymer to increasing pressure at a given temperature has an effect on its mechanical behaviour equivalent to reducing its temperature at a given pressure, (Ebewele, 2000i).

## 2.10 PROCESSING TECHNIQUES

The basic polymer processing techniques are as follows

i. Extrusion process
ii. Molding process
iii. Casting
iv. Calendaring process

v. Coating

### 2.10.1 Extrusion Process

Extrusion is a processing technique for converting thermoplastic materials in powdered or granular form into a continuous uniform melt, which is shaped into items of uniform cross-sectional area by forcing it through a die. Extrusion end products include pipes for water, gas, drains, and vents; tubing for garden hose, automobiles, control cable housings, soda straws; profiles for construction, automobile, and appliance industries; film for packaging; insulated wire for homes, automobiles, appliances, telephones and electric power distribution; filaments for brush bristles, rope and twine, fishing line, tennis rackets; parisons for blow moulding. Extrusion is perhaps the most important plastics processing method today.

Extrusion process descriptions

A simplified sketch of the extrusion line consists of an extruder into which is poured the polymer as granules or pellets and where it is melted and pumped through the die of desired shape. The molten polymer then enters a sizing and cooling trough or rolls where the correct size and shape are developed. From the trough, the product enters the motor-driven, rubber-covered rolls (puller), which essentially pull the molten resin from the die through the sizer into the cutter or coiler where final product handling takes place.The schematic representation of the various parts of an extruder consists essentially ofthe barrel, which runs from the hopper (through which the polymer is fed into the barrel at the rear) tothe die at the front end of the extruder. The screw,

which is the moving part of the extruder is designedto pick up, mix, compress, and move the polymer as it changes from solid granules to a viscous melt.

The screw turns in the barrel with power supplied by a motor operating through a gear reducer.The heart of the extruder is the rotating screw. The thread of an extruder screw is called a flight, and the axial distance from the edge of one flight to the corresponding edge on the next flight is called the pitch. The pitch is a measure of the coarseness of the thread and is related to the helix angle. The polymer is melted and pumped in the open section between the flights called the channel.The bottom of the channel is called the root of the screw. The distance between the root and the top of the flight is referred to as the channel depth. The hub and shank, located at the rear of the screw, fit into the driving mechanism. The hub acts as a seal preventing the polymer material from leaking into the machinery.

The most common and versatile extruder currently in use is the single screw extruder. Extruders are normally characterized by the bore diameters D and the length of the barrel specified as the length-to-diameter ratio, L/D. Diameters range from about 1 in. for laboratory to about 8 in. for specialized production machines. Typical L/D ratios for commercial extruders range from 20/1 to 34/1. In general, the shorter machines (L/D = 20/1 range) are used for elastomer processing while the longer ones are employed for processing thermoplastics. Screws with pitch equal to diameter are referred to as square-pitched screws and have a helix angle of 17.7°. The number of turns of the flight in a square-pitched screw gives the L/D ratio. The channel depth changes along the screw length; it is deepest at the section under the hopper and shallowest toward the tip. In a few cases where the channel depth changes gradually from one end to the other, the screw is called a constant taper screw. In most cases, however, the screw is divided into three

distinct zones each with a different channel depth. These zones are referred to as the feed, transition, and metering sections based on the differing functions.

The feed section, 1 to 10 diameters long, picks up the resin under the hopper and advances it into the externally heated barrel to begin melting.

The compression section or the transition zone, about 5 diameters long, contained the loosely packed polymer feed and in the process eliminates air pockets. It melts and forms the resin into a continuous stream of molten material. The frictional force generated between the resin, the barrel wall, and the rotating screw (viscous energy dissipation) is an important energy source for melting the resin.

The metering or pump sectionensures a uniform flow rate and generates the pressure needed to force the polymer melt through the rest of the extruder and out through the die. Screws are also sometimes described in terms of compression ratio, which is essentially the ratio of the channel depth of the first turn at the rear end of the screw to that of the channel at the last turn. Screws vary from a compression ratio of two for a low compression screw to four for a high-compression screw.Various modifications of the single screw design are available. Multi-screw extruders are also in current use for specialized application for which the single screw designs are inefficient. Examples of such applications include production of large-diameter PVC pipe and processing of heat-sensitive materials or resins that must leave the die at relatively low temperatures. Screw configuration for multi-screw extruders may involve intermeshing, co-rotating, or counter-rotating screws. Screws may also be non-intermeshing, of constant depth, or conical in shape. The barrel of the extruder is normally a long tube. It is made of a special hard steel alloy to provide resistance against wear and corrosion and has thickness sufficient to withstand high internal pressure (about 10,000 to 20,000 psi) without failure. The barrel is

equipped with systems for both heat input and extraction. The heaters are arranged in zones and are usually made of cast aluminum. Both halves of the heater are clamped to the barrel to ensure intimate thermal contact. Heat is extracted either by air or a liquid coolant. The simplest design is to mount the coolant or blower under each heater. The heaters operated manually or by automatic controllers, keep each zone of the extruders at a defined temperature. The use of microprocessors for temperature control has proved increasingly successful. The feed throat at the end of the barrel is generally jacketed for cold water circulation. This keeps the surfaces of the barrel section below the temperature that could cause premature softening of the polymer, which then sticks to and rotates with the screw. The resulting material buildup could seal off the screw channel and prevent the forward movement of the polymer — a phenomenon known as bridging.The extruder is also equipped with a gearbox, thrust-bearing mechanism, and motor. The screw derives its power for rotation from an electric motor. Power requirements are in the range of 1 horse power (hp) per 5 to 10 horse power per hour of material passing through the extruder. The electric motor has a speed of about 1700 rpm, which is too fast for a direct connection to the screw, which has speeds in the range 20 to 200 rpm. It is therefore necessary to employ a gear reducer, which provides varying screw speeds by matching the speed of the drive motor and the rotating screw. Variable speed units can usually provide a change of screw speed from 8 to 1. This enables control of extruder output since there is a direct relation between the extruder pumping rate and the screw speed.

The extruder screw is designed to develop the pressure required to pump the molten polymer through the die. This pressure also acts on the screw. Since the thrust bearing mechanism supports the drive mechanism into which fits the shank of the screw, the thrust-bearing mechanism resists the axial thrust exerted by the molten polymer on the screw. Pressures of up to

2000 psi can be developed in many extruder operations. Some polymers contain unreacted volatile monomer, moisture, and entrapped gases, which when emitted during the extrusion process could potentially contribute to poor product quality. Some extruders are provided with vents to remove these volatiles from the melt before it reaches the die. The vent is a hole in the barrel about screw diameter size, and located about three-fourths of the distance from the feed throat to the front of the barrel. In some cases, a vacuum is attached to the vent to facilitate gas removal.

The screw for a vented extruder, referred to as a two-stage screw, has a special design. The screw section under the vent has a deep channel. The section of screw before the vent can be considered a normal screw with feed, transition, and metering sections. The section following the vent consists of a short transition zone and a metering section. The channels of the metering section after the vent are deeper than those of the metering section before the vent. This coupled with the relatively higher channel depth under the vent, means that the channel is partially filled at and beyond the vent section and aids gas removal.

Different types of extrusion processes include

Pipe extrusion

In pipe extrusion, the extrudate exiting the die is vacuum-sized and quenched in a water trough. Polymer melts, being viscoelastic, recover the stored elastic energy as they emerge from the die — a process known as die swell.

In pipe extrusion, die swell must be controlled to ensure that the pipe dimensions meet standard codes.

Profile extrusion

Profile extrusion is similar to pipe extrusion. However, unlike pipes whose shape is round, hollow, and uniform, the shapes of profiles depend on the end product, which usually is the raw material for downstream processing.

Fibre extrusion

Fibres of various gauges and lengths are obtained in fiber extrusion. These can range from monofilament such as fishing lines to hundreds of continuous filaments extruded from the same die and drawn to hair-sized thickness. The continuous filaments may be crimped for added bulk or made into staples.Almost all electrical wire and cable insulation is currently done by covering the wires or cables with one or more layers of thermoplastic insulation. These, take different forms: wire strands may be covered with several layers by successive insulation; multiple pre-insulated wires may be covered to form a single cable; or several bore wires may be drawn through the die simultaneously and covered with insulation forming a ribbon cable.

Co-extrusion

In co-extrusion, two or more different materials or the same material with two different colours are extruded through the same die so that one material flows over and coats the other.Co-extrusion is used to achieve different objectives: a solid cap may be extruded over a foamed core for overall weight reduction or to obtain insulation in addition to a serviceable outer surface; for materials with surfaces sensitive to color, a virgin cap may be extruded over reground, or several

different materials may be coextruded so that each material contributes a derived property to the end product.

2.10.2 Moulding Process

Injection moulding Process

Injection moulding is one of the processing techniques for converting thermoplastics, and recently, thermosetting materials, from the pellet or powder form into a variety of useful products. Forks, spoons, computer, television, and radio cabinets, to mention just a few, are some of these products. Simply, injection moulding consists of heating the pellet or powder until it melts. The melt is then injected into and held in a cooled mold under pressure until the material solidifies. The mould opens and the product is ejected. The injection moulding machine must, therefore, perform essentially three functions:

i.Melt the plastic so that it can flow under pressure.

ii.Inject the molten material into the mould.

iii. Hold the melt in the cold mould while it solidifies and then eject the solid plastic.

These functions must be performed automatically under conditions that ideally should result in a high quality and cost-effective part. Injection moulding machines have two principal components to perform the cyclical steps in the injection moulding process. These are the injection unit and the clamp unit which are describe as follow:

The injection unit

The injection unit essentially has two functions: melt the pellet or powder and then inject the melt into the mold. It consists of the hopper, a device for feeding process material; a heated cylinder or chamber where the material is melted; and a device for injecting the molten material into the mould. In the early days when the amount of processed material was relatively small, the two functions of melting and injecting the polymer were accomplished by using a simple plunger machine. In this system, a measured volume of the plastic material is delivered into the heated cylinder from the hopper while the ram is retracted. At the beginning of the injection cycle, the plunger pushes forward and forces the material through the heated cylinder compacting it tightly behind and over the centrally located spreader or torpedo. The material is melted by heat convection and conduction. The sustained forward motion of the plunger forces the melt through the nozzle of the cylinder into the mold.In the plunger-type machine, material flow in the cylinder is essentially laminar. Consequently there is hardly any mixing in this system and, as such, large temperature gradients exist in the melt, and color blending is thus problematic. Also, as a result of the friction between the cold resin pellets in the neighborhood of the hopper and the barrel walls, a considerable loss of pressure, up to 80% of the total ram pressure, occurs. This necessitates long injection time. As indicated above, the resin is melted by heat conduction from the walls of the cylinder and the resin itself. Since plastics are poor heat conductors, high cylinder temperatures are required to achieve fast resin plasticisation. This can result in the degradation of the material. To avoid such possible material deterioration, the heating of the cylinder is limited, and this also limits the plasticizing capacity of plunger-type injection machines.Today, the plunger has been replaced almost totally by the plasticating screw.The plasticating screw consists basically of three sections: the feed, the transition zone, and the metering section.Melting normally starts halfway down the length of the screw at which point

the depth of the screw flights decreases initiating the compression of the melt. This marks the beginning of the transition zone, which terminates at that metering section — the point where the depth of the flights is minimum. A number of screw configurations exist, including the mixing screw, the marblizing screw, and that with decompression zone geometry to permit venting and ridding the melted material of volatiles.There are essentially two methods of using the plasticating screw. The first is the screw-plunger system also called the two-stage or screw-pot system. The screw rotates in the heated barrel and consequently plasticizes the polymer material. The plasticized material is then transferred into a second heated cylinder from which it is injected into the mold by a plunger. In the second approach developed in the mid-1950s**,** a reciprocating screw is employed. As the screw rotates, it picks up the material from the hopper. The material is melted primarily by the shearing action of the screw on the resin. The electrical heating bands attached to the barrel essentially provide start-up and compensate for heat losses. The rotation of the screw moves the melted material forward ahead of the screw. The pumping action of the screw generates back-pressure, which forces back the screw, the screw drive system, and the hydraulic motor when enough melted material required for a single shot has accumulated in front of the screw. As the screw moves backward, it continues to turn until it hits a limit switch, which stops the rotation and backward movement. The location of the limit switch is adjustable and determines the shot size. Meanwhile the clamp ram has moved forward with the movable platen and closed the mould. When the backward movement of the screw is stopped, the hydraulic cylinders bring the screw forward rapidly and inject the melted material through the nozzle into the mold cavity. A ball check or check ring on the end of the screw (valve) prevents the melt from leaking into the flights of the screw during injection. Consequently, most of the melt is forced into the mold. The mould is cooled and the part solidifies. At the end of the

predetermined period, the mould opens as the movable platen returns to its initial position and the part is ejected. The screw starts rotating, beginning the next cycle. The plasticating screw-type machines obviate most of the problems associated with the plunger system. The resin is heated mainly by viscous heat generation as opposed to thermal conduction from cylinder walls. In addition, in contrast to the block of material in the barrel in plunger-type machines, only a thin layer of material exists between the screw and the barrel walls and thus the resin is heated faster. Also in the screw-type machines, the melt is thoroughly mixed. Consequently, these machines produce a melt with a more uniform temperature and homogeneous color, high injection pressures, faster injection speeds and shorter cycles, and therefore higher production rates.

The Clamp Unit

The clamp unit or press end of the injection moulding machine performs three functions: opens and closes the mould at appropriate times during the molding cycle; ejects the moulded part; and provides enough pressure to prevent the mould from opening due to the pressure developed in the mold cavity as it is filled with the melt by the injection unit. Injection pressures in the plasticating cylinder can range from 15,000 to 20,000 psi in a given system. As a result of possible pressure drops in the cylinder and the nozzle, the effective pressure within the mould cavity may be reduced to 25 to 50% of this value. Consequently, the force needed to resist the premature opening of the mould and obtain an acceptable part can be quite large. For example, assuming a 50% pressure drop and using the upper possible pressure in the cylinder stated above, the melt pressure in the mold cavity becomes 10,000 psi. This translates into a clamp force of 5 tons/in$^2$ of the projected area of the part. However, as a result of greater degree of homogenisation achievable in screw-type machines, the clamp tonnage required in these

machines is generally less than in plunger-type machines. The halves of the mould are attached to the platens, one of which is stationary and one of which moves as the clamp mechanism is opened or closed. Molds are generally designed so that the ejection side of the mould (mould core) is on the movable platen and the injection side of the mold (mold cavity) is on the stationary platen, which must provide an entry for the nozzle of the plasticizing chambers. When the mold opens, the movable platen must be moved sufficiently for the part to be ejected. Shrinkage usually accompanies part solidification and this result in the part sticking to the core as the mold opens. Consequently, the movable platen is provided with an ejector or knockout system to eject the part. The ejector usually consists of a hydraulically actuated ejector plate mounted off the back face of the movable platen. The ejector system causes the knockout plate to change its location relative to the rest of the mold. The ejector pins attached to this plate push against the moulded part and eject it from the mold. The force required to eject the part is usually less than 1% of the nominal clamp force: its magnitude depends on the part geometry, material, and packing pressure. There are essentially two categories of clamp systems for moving and locking the movable platen. These are the mechanical (toggle) and hydraulic systems. The toggle system, which is used mainly in small tonnage (about 500 tons) equipment, is relatively inexpensive but requires good maintenance because wear reduces the clamping force. Hydraulic systems, used primarily in medium and large equipment (1500 to 2000 tons), are relatively slow acting but have the advantage of providing virtually limitless pressure selection, which can be followed continuously with a pressure gauge. Machine flexibility permits the necessary adjustment to match mold thickness and settings.

Blow Moulding

Blow moulding is a process used extensively for the production of bottles and other hollow plastic items with thin walls. Blow-moulded objects may range in size from less than 1oz to a few hundred gallons.

Process description

The blow moulding process consists of a sequence of steps leading to the production of a hollow tube or parison from a molten thermoplastic resin. This is then entrapped between the two halves of a mold of the desired shape. Air, usually at about 100 psi, is blown into the soft parison, expanding it against the contours of the cold mold cavity. The part is cooled and removed from the mould, and where necessary the excess plastic material or flash accompanying the moulded part is trimmed and reclaimed for reuse.The blow moulding process therefore involves essentially two properly synchronized operations: parison formation from the plastic material and blowing the parison into the shape of the desired part.

There are two techniques for plasticizing the resin for parison formation. These are extrusion blow moulding (which is the most common method and which is characterized by scrap production) and injection blow moulding. The latter process is versatile and scraps free and is beginning to be more understood and accepted by processors.

Extrusion Blow Moulding

In extrusion blow molding, an extruder, as described in Section II, is used to plasticize the resin and form the parison. The process may be continuous or intermittent. In the continuous process, a continuous parison is formed at a rate synchronized with the rates of part blowing, cooling, and removal. Two general mold clamp mechanisms are used for part formation from the extruded parison. In the first arrangement or shuttle system, the blowing station is situated on one or both

sides of the extruder. As soon as an appropriate length of parison is extruded, the clamp mechanism moves from the blowing station to a position under the die head, captures and cuts the parison, and then returns to the blowing station for part blowing, cooling, and removal. This ensures that there is no interference with parison formation. In the second or rotary system, a number of clamping stations are mounted on a vertical or horizontal wheel. As the wheel rotates at a predetermined rate, blowing stations successively pass the parison head(s) where it is entrapped for subsequent part formation. In this case, parison entrapment and blowing, part cooling, and removal occur simultaneously in a number of adjacent blowing stations.In the intermittent extrusion process, molding, cooling, and part removal take place under the extrusion head. An extruder system, which may be of the reciprocating screw, ram accumulator, or accumulator head type, extrudes the parison in a downward direction where it is captured at the proper time between the two halves of the mould. The part is then formed and ejected and a new cycle begins.As the name suggests, in the intermittent extrusion blow moulding process, parison formation is not continuous. For example, with the reciprocating screw machine, after the parison is extruded, melt is accumulated in front of the screw causing a retraction of the screw. After the moulded part has cooled and the mould opens and ejects the part, the screw is immediately pushed forward by hydraulic pressure, forcing the melt into the die to initiate the formation of the next parison.

Injection Blow Moulding

The injection blow moulding process is a non-continuous cyclic process consisting essentially of two phases. In the first phase, a preform is molded by injecting melted plastic into a steel mould cavity where it is kept hot and conditioned. In the second or subsequent phase, the preform is metered into the blow mould where the blowing operation takes place to form the final part. The

major advantages of injection blow moulding are the quality of the moulded part and productivity. There is no flash production. Therefore, the moulded part neither has a pinch-off scar from flash nor requires additional trimming or other finishing steps for waste retrieval. Also, the moulded parts show hardly any variation in weight, wall thickness, and volume from the accurately moulded preform. However, only blow-moulded parts with limited size and shape and without handles are feasible with the injection blow moulding process.

Rotational Moulding

Process description

Rotational moulding is a process used for producing hollow, seamless products having heavy and/or complex shapes. In rotational molding a premeasured amount of powder or liquid polymer is placed in the bottom half of the mould, and the two halves of the mold are locked together mechanically. The mold is then rotated continuously about its vertical and horizontal axes to distribute the material uniformly over the inner surface of the mould. The rotating mould then passes through a heated oven.As the mould is heated, the powdered polymer particles fuse forming a porous skin that subsequently melts and forms a homogeneous layer of uniform thickness. In the case of a liquid polymer, it flows over and coats the mould surface and then gels at the appropriate temperature. While still rotating axially, the mould passes into a cooling chamber where it is cooled by forced air and/or water spray. The mould is then moved to the work station and opened, and the finished solid part whose outside surfaces and contour faithfully duplicate those of the inner mold surface is removed. The mould is recharged for the next cycle.

PROCESS VARIABLES

Different types of heating systems, including hot air, molten salts, or circulation of oil through a jacketed mold have been used. The essential requirement of any heating system is to ensure that the mold is heated uniformly and at a properly controlled rate so that the desired part thickness is obtained without causing resin degradation. Given the potential hazards and maintenance problems associated with the use of molten salts, the use of hot oil has gained wide commercial acceptance because of the relatively cleaner, cheaper, and safer operation involved.While the heating cycle has virtually no effect on the properties of the finished part, the cooling rate determines part shrinkage, final density, brittleness, and other physical properties. Mould cooling is accomplished by the use of forced air and/or application of water spray.Rotational moulding machines vary from the simple one-arm rotor cast system with capability for producing parts of up to 20 gallons (gal) size to the industrially predominant three-arm machines that are capable of producing up to 5000 gal capacity tanks. In the latter case, each arm is always in one of the three stations: load-unload, oven, or cooling. More recently, shuttle-type machines with moulds mounted on large self-driven shuttle carts have been developed. The carts move on tracks from the oven to the cooling chamber. These machines can make products of much larger capacities. Rotational moulding machines with micro-processor controls and other solid-state devices for regulating operating variables such cycle time, oven temperature, rotational speed ratio (ratio of the speed of major to minor axis), and fan and water on–off times are now available.The rotational moulding operation involves neither high pressure nor shear rates. In addition, precise metering of materials is not crucial. Therefore, rotational moulding machinery is relatively cheap and has a more extended lifetime. Other advantages of rotational moulding include favourable cost–performance (productivity) ratio, absence of additional finishing operations even of

complex parts, minimal scrap generation, and capability for simultaneous production of multiple parts and colours.

THERMOFORMING

Thermoforming is a process for forming moderately complex shaped parts that cannot be injection molded because the part is either very large or too expensive or has very thin walls. It consists essentially of two stages: elevation of the temperature of a thermoplastic sheet material until it is soft and pliable and forming the material into the desired shape using one of several techniques.

PROCESS DESCRIPTION

Thermoforming techniques may be grouped into three broad categories: vacuum, mechanical, and air blowing processes.

Vacuum Forming

In vacuum forming process,the plastic sheet is clamped in place mechanically and heated. A vacuum is then placed beneath the hot elastic sheet, and this makes atmospheric pressure push the sheet down onto the contours of the cold mould. The plastic material cools down, and after an appropriate time the cooled part is removed.

Mechanical Forming

In this case, a hot sheet is stretched over a mould or matched molds without the use of air or pressure.For example, in matched mould forming, the heated sheet is clamped over a female mold or draped over the mould force (male mould). The two moulds are then closed. The

resulting part has excellent dimensional accuracy and good reproduction of the mould detail, including any lettering and grained surfaces.

Air Blowing Process

Here compressed air is used to form the sheet. In one variation, a plastic sheet is heated and sealed across the female cavity. Air at controlled pressure is introduced into the mould cavity.This blows the sheet upward into an evenly stretched bubble. A plug which fits roughly into the mould cavity descends on the sheet. When the plug reaches its lowest possible position, a vacuum or, in some cases, air under pressure is used to complete part formation.From the foregoing discussion, it is evident that the basic steps in the thermoforming process involve a sequence of operations: loading the sheet or web through the system in increments and heating, forming, and cooling. Other secondary functions that may be integrated into the process include trimming and other finishing operations. Thermoforming machinery is categorized on the basis of the arrangement for performing these operations. In single station machines, the loading, heating, forming, cooling, and unloading operations are performed in succession. Consequently, even though these machines are versatile, they are characterized by comparatively long cycle times. With in-line machines, which are quite popular in the packaging industry, the different operations are performed simultaneously in a multi-station in-line system. In this case, therefore, the cycle time is determined by the longest operation in the entire process. The third category of thermoforming machines is the rotary type, which is supported on a horizontal circular frame that has three work (and possibly other secondary stations for the loading– unloading, heating, and forming (possibly secondary) operations. By rotating the cut sheets sequentially from station to station, the rotary machine configuration is well suited for high production rates.

Moulds for the thermoforming process may be made of wood, metal, or epoxy and are relatively cheap.They are provided with vents to allow trapped air to escape and release possible pressure buildup.Temperature control, as we shall see in the following discussion, determines part quality. It is, therefore, crucial that mould temperature is controlled properly. The mould is consequently provided with channels for the passage of the cooling liquid.

Process variables

Thermoplastic materials, in general, can be stretched when hot. However, the degree of success in forming a part from a hot, stretched sheet material depends on the particular resin, its molecular weight, and processing conditions like forming temperature and speed. Recall from section 2.10.3, that the thermal response of thermoplastic polymers depends first on whether the material is amorphous or crystalline and to some extent on their molecular weights. When heated, crystalline polymers undergo a rather abrupt phase transformation from the solid to the fluid state, while amorphous polymers undergo a more gradual transformation. For a given resin, the degree of fluidity depends on molecular weight and the processing temperature. The higher the molecular weight, the higher the melt strength and consequently the greater the capacity of the material to be deep-drawn, which is a necessary condition for the proper formation of intricate parts. On the other hand, materials that are too fluid at the forming temperature are susceptible to tearing, leading to the production of bad quality parts. Given the influence of forming temperature on part quality, it is necessary to ensure that sheets have a uniform temperature distribution. This also calls for a uniform sheet thickness. A variation in sheet thickness causes a non-uniform sheet temperature distribution resulting in uneven pulling and possible tearing of the sheet. It is also essential to recognize that variation of shrinkage with

sheet orientation can generate forming problems. If there is excessive differential shrinkage due to sheet orientation, the pull from the clamping frames during forming becomes unbalanced and the sheet could be pulled out.

Compression and Transfer Moulding

The two most widely used methods for molding thermoset are compression and transfer molding. Generally, thermosets undergo a permanent set, i.e., become essentially insoluble and infusible under the action of heat. Consequently, techniques for fabricating thermosets must take due cognizance of and make allowance for the fact that sprues, runners, and gates are not reusable and therefore constitute rejects.

Compression Moulding

In compression moulding, a pre-weighed amount of material is loaded into the lower half of a heated mould or cavity. The force plug (plunger) is lowered into the cavity, and pressure, which can range from 20 to 1000 tons, is applied to the powder. Under heat and pressure, the powder melts and flows into all parts of the mould cavity; the resin cross-links thus becoming irreversibly hardened. After an appropriate time, the mould is opened and the part is ejected while still hot (usually under gravity) and allowed to cool outside the mould.The machinery for compression molding is relatively simple, consisting essentially of two platens, which when brought together, apply heat and pressure to the mold material to form a part of desired shape. The platens move vertically, with the cavity usually mounted at the bottom so moulding material can be loaded into it. Material may also be a preform, in which case it has been preheated. Material flow, cure time, and the ultimate properties of the moulded part depend on the mould

temperature, which therefore must be adequately controlled. A number of heating systems are employed for heating the moulds. Steam heating provides uniform mold temperature but is limited to temperatures below 200°C. Electrical heating is both clean and easy and enjoys wide usage. Circulated hot oil also provides uniform heat. Most thermosets emit volatile gases or moisture during cure, and escape avenues must be provided for such volatiles to facilitate processing and obtain good quality parts. This is usually accomplished by opening the mould slightly. With modern compression moulding machines various degrees of automation for feeding the material and ejecting the molded part are possible. This is achieved by the use of microprocessor controllers.One of the major advantages of compression molding is that it is relatively inexpensive because of its simplicity. Also, since there are no sprues, runners, and gates, material waste is reduced considerably.

The consistency of part size is good and the absence of gate and flow marks reduces finishing costs.

Transfer Moulding

In transfer moulding, a measured charge of preheated thermoset material is placed in a separate or auxiliary heated chamber called the pot. A plunger is then used to force the molten material out of the pot through the runner system into the closed mold cavity where curing occurs. As the material enters the mould, the air from the mould cavity escapes through vents located strategically on the mould.At the end of the cure cycle, the entire shot, including the gates, runners, sprues, and excess material remaining in the pot (referred to as cull) is ejected simultaneously with the moulded part. If held for too long in the pot or cylinder, the thermosetting material could cure prematurely into a solid mass.Consequently, only sufficient material for a single shot is loaded at one time. In addition, preheating the material is necessary

in transfer moulding. When cold, the material flows relatively slowly. In this case, the first material to enter the cavity could cure prematurely resulting in overall improper material mix.This can result in poor product quality in terms of the surface finish and mechanical properties.Transfer moulding has comparatively shorter cycle and loading times than compression moulding. Thick sections that cure evenly can be moulded: however, mould costs are generally higher, and greater volumes of scrap are generated because of the presence of gates, runners, and spruces. In screw injection moulding of thermoplastics, the viscous heat generated assists in melting the resin material: during processing the resin is always held in the cylinder during and between shots. However, with thermoset, to avoid resin pre-curing, not only must the barrel and material temperatures be carefully controlled, the resin cannot be held at high temperature for any length of time before moulding.

### 2.10.3 Casting

In the casting process, a liquid material is poured into a mold and allowed to solidify by physical (e.g, cooling) or chemical (e.g., polymerisation) means resulting in a rigid object that generally reproduces the mould cavity detail with great fidelity. A large number of resins are available and a variety of moulds and casting methods are used in casting processes. Therefore, the choice of liquid material, mould type, and casting technique is determined by the particular application.

#### Process description

In casting processes, the resin material is added with an appropriate amount of hardener, catalyst, or accelerator, mixed manually or mechanically, and then poured into a mould, which is normally coated with a mould-release agent. Air is removed if necessary and the resin is allowed

to solidify. The casting process is relatively slow and employs comparatively cheap equipment. Moulds for casting processes are fabricated from a wide variety of materials, including wood, plaster and clay, glass, metal, rubber and latex (for flexible molds), and plastics. To facilitate the removal of the cast part from the mould, mould releasing agents such as high melting waxes, silicone oils, greases, and some film-forming agents are used to coat the mold. Among other considerations, the choice of mold-release agents is based upon the absence of interaction between the resin system and the release agent. The setting of the resin material is generally exothermic and is usually accompanied by a reduction in volume. For example, in the casting of acrylic, the amount of heat evolved is about 13.8 kcal/mol, while the volume reduction can be as large as 21%. The quantity of heat liberated depends on the size, but is independent of the shape of the casting. However, the rate of heat dissipation depends both on the size and shape of the casting.Therefore, different methods have to be employed in casting thick or thin sections. Thin sections can be cast at room temperature with minimal possibility of cracking of the casting since heat can be dissipated rapidly. On the other hand, with thick sections, particularly those whose shapes limit the rate of heat removal, large temperature gradients exist between the interior and exterior sections of the casting.This generates internal stresses and enhances the possibility of cracking of the cast part. In this case, therefore, where the quantity of heat liberated cannot be changed, the rate of heat dissipation is controlled by carefully selecting the hardener and a mold material with appropriate thermal properties and by using a possible stepwise increase in casting temperature. To reduce shrinkage and the attendant built-in stresses in the cast part, flexibilizers, diluents, flexibilized resins or hardeners, or fillers are used.

CASTING OF ACRYLICS

Acrylic castings are prepared with polymers derived from methacrylic ester monomers. They usually consist of poly-(methyl methacrylate) or its copolymers as the major component modified with small amounts of other monomers. Acrylic castings are made by heating the monomers or partially polymerized syrups containing 0.02 to 0.1% radical initiator (e.g., peroxide or azo-bis-isobutyronitrile) in a mould.Syrups are prepared by dissolving finely divided polymer in the monomer. As indicated earlier, the polymerization reaction involved in the acrylic casting process is exothermic and is usually accompanied by about 15 to 21% volume shrinkage. Because of the exothermic nature of this reaction, measures are usually taken to deal with the problems of heat removal and residual stresses in the casting.The outstanding optical properties of acrylic casting make acrylic sheets invaluable in applications where excellent transparency and resistance to UV are imperative. The fabrication of acrylic sheets therefore predominates in the acrylic casting process. Cast acrylic resins also account for most of the embodiments used for decorative or study purposes. In this case, hard polymers of ethyl or methyl methacrylate are used. Rods and tubes are also prepared from acrylic castings.

CASTING OF NYLON

The nylon casting process consists basically of four steps. These are the melting of the monomer, which is usually lactam flakes, the adding of the catalyst and activator, the mixing of the melts, and the casting process itself. Co-catalyzed anionic polymerisation is currently the most widely used nylon casting method. The co-catalysts are strong bases and their salts with imides and lactams.Since absorbed water can cause catalyst decomposition and hence incomplete polymerization and since lactam monomer flakes are highly hygroscopic, the melting of monomer is carried out under appropriately controlled temperature and humidity conditions. All additives are also completely dried and then mixed with the monomer in stainless steel vessels

while flushing with inert gas under thermostatically controlled temperature. Molds can be of the single type fabricated from silicone rubber, epoxy, or sheet steel or the more expensive tool steel used in tight tolerance cast-to-size parts casting.The nylon casting process is relatively more economical and is a more practical technique for the production of large and thick parts than comparable extrusion and injection molding processes. In addition, the crystallinity and molecular weight of cast nylon are higher than those of extruded or moulded nylon. Consequently, cast nylon has a much higher modulus and heat deflection temperature, improved solvent resistance, and better hygroscopic characteristics and dimensional stability, (Ebewele, 2000j).

# CHAPTER THREE

# MATERIALS AND METHODS

## 3.1 Equipment/Materials

Table 3.1 Materials and their sources

| | Materials | Sources |
|---|---|---|
| 1. | Soybean oil | Grand company Jos, Plateau State. Available in Sahad store, Wuse market Abuja. |
| 2. | Wij's Solution | Steve-More chemical LTD Samaru, Zaria |
| 3. | Starch indicator | Steve-More chemical LTD Samaru, Zaria |
| 4. | Sodium thiosulphate | Steve-More chemical LTD Samaru, Zaria |
| 5. | Potassium iodide | Steve-More chemical LTD Samaru, Zaria |
| 6. | 40% Hydrogen peroxide | Steve-More chemical LTD Samaru, Zaria |

| | | |
|---|---|---|
| 7. | Glacial acetic acid | Steve-More chemical LTD Samaru, Zaria |
| 8. | Sulphuric acid | Steve-More chemical LTD Samaru, Zaria |
| 9. | Nitrogen gas | COSMAN Gas company, Samaru, Zaria |
| 10. | Hydrogen bromide | Steve-More chemical LTD Samaru, Zaria |
| 11. | Crystal violet indicator | Steve-More chemical LTD Samaru, Zaria |
| 12. | Chlorobenzene | Steve-More chemical LTD Samaru, Zaria |
| 13. | Potassium acid phthalate | Steve-More chemical LTD Samaru, Zaria |
| 14. | Polystyrene | Polymer department, NILEST |
| 15. | Chloroform | Steve-More chemical LTD Samaru, Zaria |

Table 3.2 Equipment and sources

| S/No. | Equipment | Manufacturer/Model | Source |
|---|---|---|---|
| 1. | Tensile strength tester | Monsanto Tensometer (type 'W') S/No. 9875 made in U.K | Mechanical Engineering Department, A.B.U., Zaria. |
| 2. | FTIR Spectrometer | Model = NICOLET IS10, made in U.S.A | Multi-user research lab. Chemistry department, A. B.U., Zaria. |
| 3. | Viscometer | Ostwald-Fenske type | NILEST, Zaria. |
| 4. | Reactor set-up | See appendix 2 | NILEST, Zaria. |
| 5. | Casting mould | Locally fabricated | Mechanical Engineering department, A.B.U., Zaria |

Table 3.3 Apparatus and sources

| S/No. | Apparatus | Manufacturer/Model | Sources |
|---|---|---|---|
| 1. | Weighing balance | S. Melttler / FA 2104 | NILEST, Zaria. |
| 2. | Glass wares | Locally fabricated | Steve-moore chemical, LTD, Zaria |

## 3.2 METHODS

### 3.2.1. Iodine number determination of soybean oil (Wij's solution method)

0.216g of soybean oil sample was weighed accurately into a conical flask. 10ml of carbon tetrachloride ($CCl_4$) and 25ml of Wij's solution were added successively into the conical flask containing the soybean oil sample. Then, the flask was vortexed and allowed to stand for 1hr in the dark cupboard. After then, 15ml of 10% potassium iodide was added, followed by addition of 50ml of distilled water and 1ml of 10% starch solution. The mixture (total content of the conical flask) was titrated against 0.1*N* solution of sodium thiosulphate ($Na_2S_2O_3$) to the disappearance of blue-black colour, indicating an end-point.

Blank titration was carried out in the same procedures except the absence of soybean oil sample in the total content of the mixture contained in the conical flask.

Thus, the iodine value (IV) is calculated as follows

$$IV=\frac{(a-b)\ x\ N\ x\ 1.269\ x\ 100}{W} \quad (36)$$

where: b = average blank titre value

a = average sample titre value (mL)

*N* = Normality of sodium thiosulphate (Mol/$dm^3$)

w = weight of soybean oil sample (g)

(AOCS Cd 3 –35, 1997)

3.2.2 Epoxidation of Soybean Oil (conventional method as reported by Taydee*t al*, 2012)

Set-up description (see plate 1)

The 3-neck round bottom flask was placed on a thermally regulated hot plate magnetic stirrer in a fume cupboard. The central neck of the round bottom flask was fitted with the reflux condenser vertically. On the reflux condenser, is clamped the separating funnel for gradual in-let of hydrogen peroxide. The adjacent neck was fitted with thermometer, while the other neck was fitted with quick fit funnel for inlet of sample/chemical reagents.

Synthesis:

Stoichiometric molar ratios of 2:3:1 corresponding to soybean oil sample, hydrogen peroxide and glacial acetic acid respectively were adopted.

Procedure:

100g of soybean oil sample was weighed into the round bottom flask and subjected to heating till temperature reached $45^{O}C$. (This was to energized the carbon-carbon double bonds – site of epoxidation reaction). Then, appropriate amount of glacial acetic acid was added. The addition of glacial acetic acid decreased the reaction temperature to $40^{O}C$. While stirring at high frequency with magnetic stirrer, 2% $H_2SO_4$by total volume of glacial acetic acid and hydrogen peroxide was added to catalyzed the system. The addition of $H_2S_2O_4$ catalyst caused the black colouration of the mixture and induced exothermic reaction to a temperature of $55^{O}C$. On continuous stirring at higher frequency with effective refluxing system, appropriate amount of hydrogen peroxide was gradually charged into the flask drop by drop via clamped separating funnel fitted on condenser. The gradual addition of hydrogen peroxide marked the disappearance of black colouration of the mixture to pale-yellow and on-set of highly exothermic reaction to a controlled temperature of $65^{O}C$ using nitrogen gas at a pressure of 1 bar. The total reaction time was 5hrs. After 5hrs of un-interrupted reaction condition, the mixture was allowed to cool in air, poured in a separating funnel and stood for 24hrs for effective separation.

### 3.2.3 FT-IR Characterisation of Oil Samples: (a) Soybean Oil (b) Epoxidized SoybeanOil (ESO) (c) Modified Epoxidized Soybean Oil Sample (MESO)

The machine was first calibrated before use. The KBr plate was cleaned with ethanol for various characterisation. The ESO sample was smeared on one side of the plate and sandwiched on the other side. The plate was later tittered on the sample holder and then inserted into the sample chamber. The spectral display was taken.

3.2.4 Determination of Epoxy Content or Yield (I.E Oxirane Oxygen) of the Epoxidized Vegetable Oil

0.55g of epoxidized soybean oil was weighed into a 5 conical flask. Then, the sample was dissolved in 10 mL of glacial acetic acid. 5 drops of crystal violet indicator was added while stirring using stirring bar. And it was then, titrated with 0.1M HBr solution to a blue-green end-point that persist for 30 seconds.

Calculation,

$$\text{Molarity of HBr} = \frac{\text{Mass of potassium acid phthalate,g}}{0.2042 \text{ x mL HBr solution}} \quad (37)$$

$$\text{Oxirane oxygen, \%} = \frac{\text{mL HBr to titrate sample x M x 1.6}}{\text{Mass of sample,g}} \quad (38)$$

Where;

M = Molarity of HBr solution.

(AOCS Cd 9-57, 1997)

### 3.2.5. Thermal Curing of Epoxidized Soybean Oil Sample (MESO Synthesis)

The epoxidized soybean oil was charged into a 3-neck round bottom flask, heated to a controlled temperature of $75^{O}C$ for 4 hrs while continuous stirring and refluxing. Gelation took place.(See appendices 3 and 4 for ESO and MESO respectively)

### 3.2.6. Solution blending of polystyrene and MESO

Procedure

10g, 9g, 8g, 7g, 6g, 5g and 4g of polystyrene were weighed in different labelled sample bottles respectively. An appropriate volume (i.e the proportional amount (mL) of chlorobenzene required for complete dissolution of the weighed polystyrene) was added into each of the sample bottle containing the weighed polystyrene sample and was allowed to dissolve for 5hrs.

After dissolution, 1g, 2g, 3g, 4g, 5g, and 6g of MESO were weighed into their respective sample bottles as to exist in a definite ratio combination. Each combination was thoroughly stirred using stirring bar to ensure complete miscibility in chlorobenzene.

### 3.2.7. Processing Technique (Casting)

Mould type used: metal mould of dogged bone shapes with the same dimensions 5mm thick, 20mm width on both edge, 10mm width of middle part, 120mm length of entire sections (40mm for each of the 3-section).

The mould was sealed to prevent slippages of one blend ratio into the other. The blends were then casted into their respective labelled mould and were allowed to dry in air for 10 days. After that, the films of dogged bone shapes were obtained.

### 3.2.8. Stress-Strain Experiment

The dogged bone shape of the each blend was clamped at both edge and then drawled till there was a fall in the fudicial mark on tensometer. The graft paper was taken and the readings noted.

(ASTM D590)

### 3.2.9. Viscosity measurements

$0.01g/dm^3$ of various blend compositions were prepared. The solutions were diluted to different concentrations. 10ml of each blend's concentration was poured into "A" part of the viscometer using string and was blow into the "B" compartment using the pressure pump. The time (T) taken for each blend concentration to move from upper fudicial mark of "B" compartment to lower fudicial mark after passing through a capillary tube was noted. Theviscometer measurements were done in a water bath of $23^OC$.

# CHAPTER FOUR

# RESULTS

Table 4.1 gives the physicochemical characterization of soybean oil and epoxidized soybean oil

| | |
|---|---|
| Iodine number of soybean oil | 149.8 |
| % oxirane-oxygen content of epoxidized soybean oil | 9.77 |

Table 4.2Mechanical properties of the blends

| % PS/MESO Blend | Strain | Tensile stress ($10^2$) ($Nm^{-2}$) | Young's modulus ($10^2$) ($Nm^{-2}$) | % elongation-at-break |
|---|---|---|---|---|
| **10:0** | 0.81 | 3810 | 4704 | 81 |
| **9:1** | 0.27 | 2170 | 8037 | 27 |
| **8:2** | 0.37 | 3030 | 8189 | 37 |
| **7:3** | 0.63 | 2012 | 3194 | 63 |

| | | | | |
|---|---|---|---|---|
| **6:4** | 0.29 | 4286 | 14779 | 29 |
| **5:5** | 0.39 | 2367 | 6069 | 39 |
| **4:6** | 0.52 | 1423 | 2737 | 52 |

The table showed the tensile strength, Young's modulus and Elongation-at-break of various PS/MESO blends' composition.

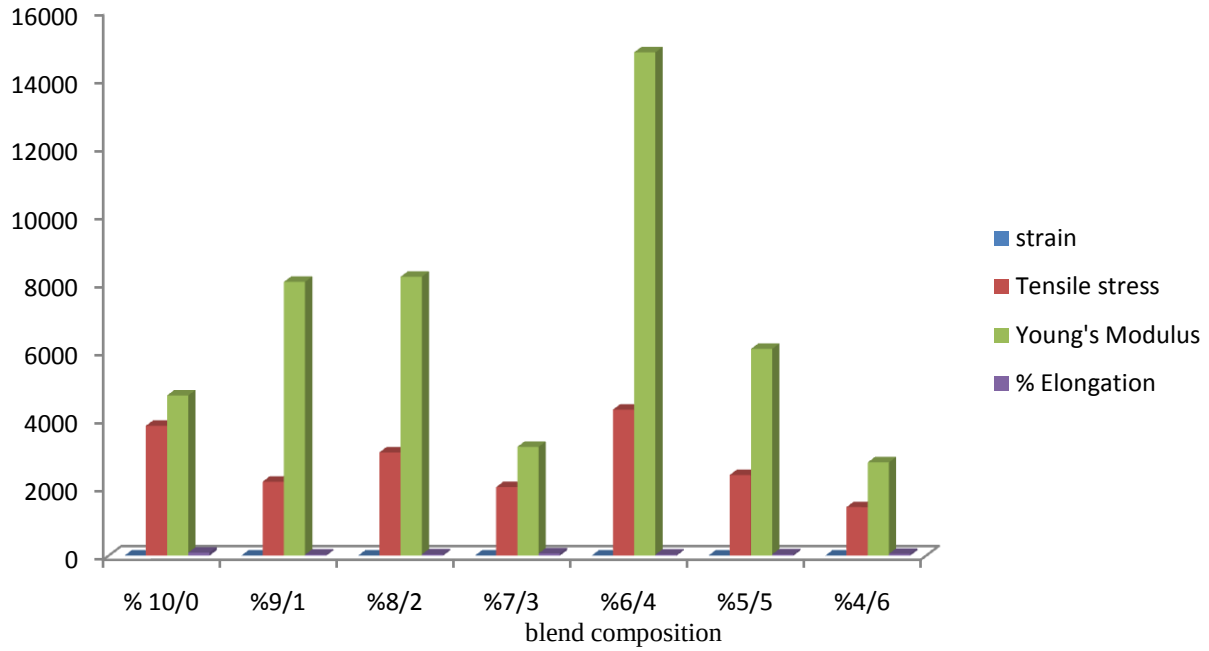



Fig. 4.1 Bar chart representation of mechanical properties against blend compositions

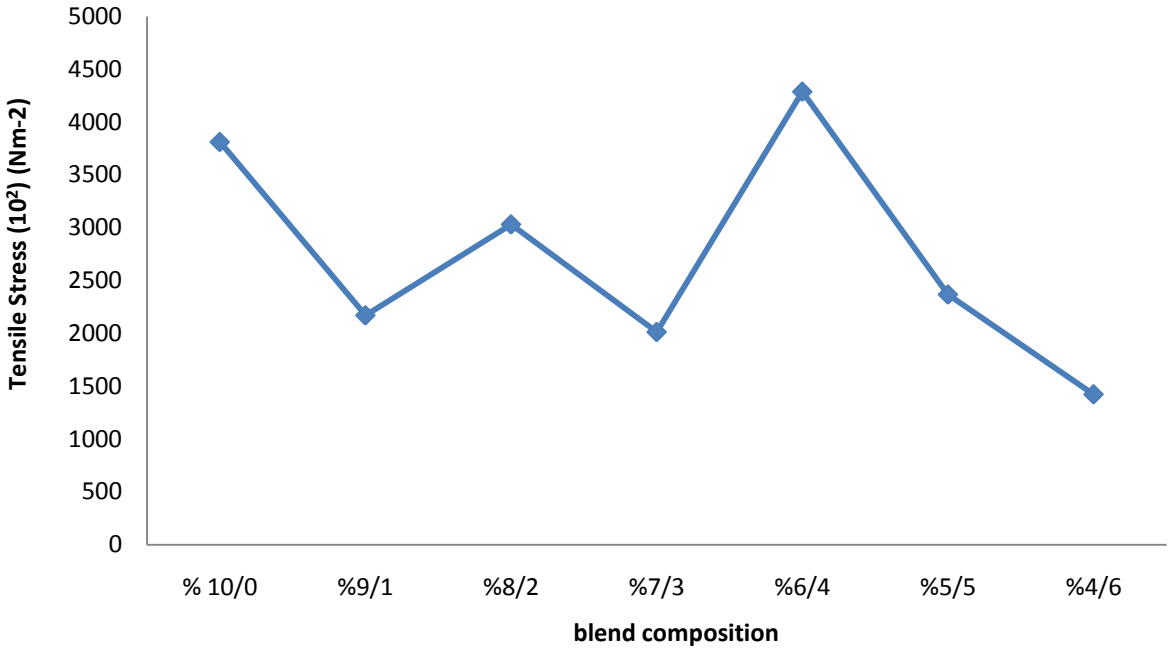



Fig. 4.2Tensile strength against blend composition

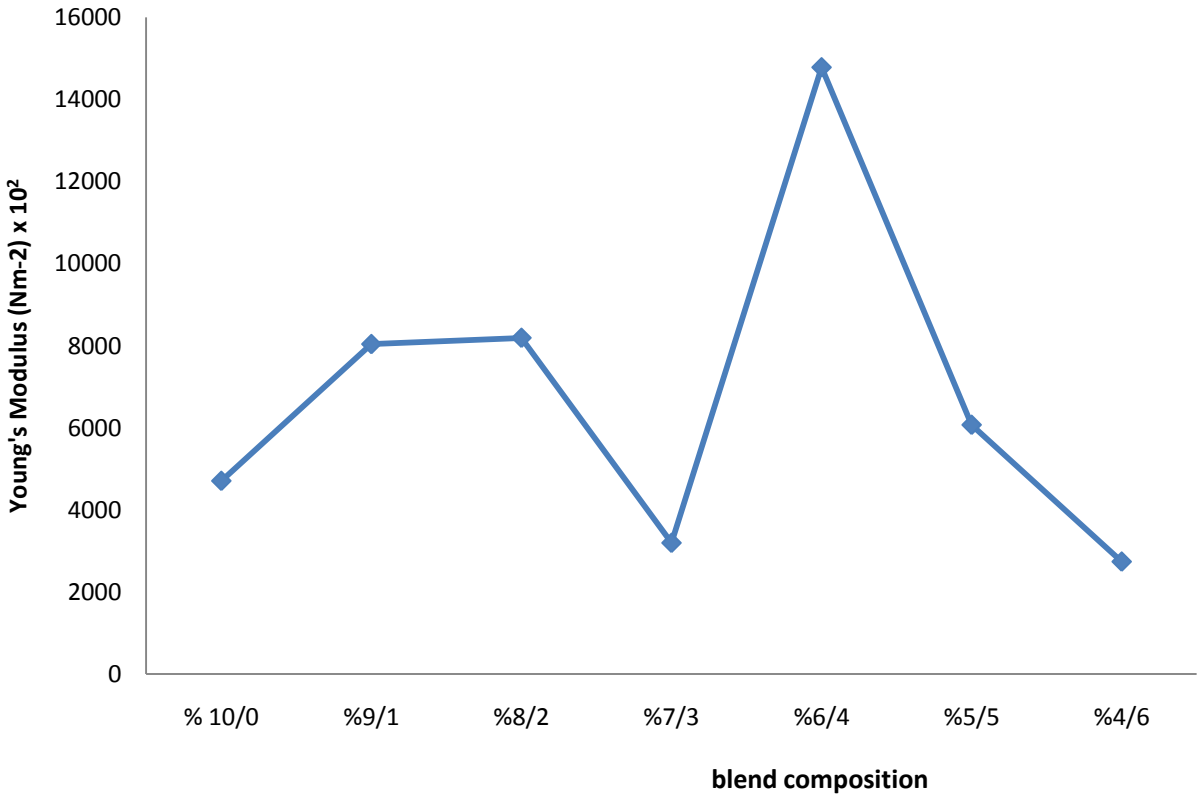


Fig. 4.3 Young's modulus against blend composition

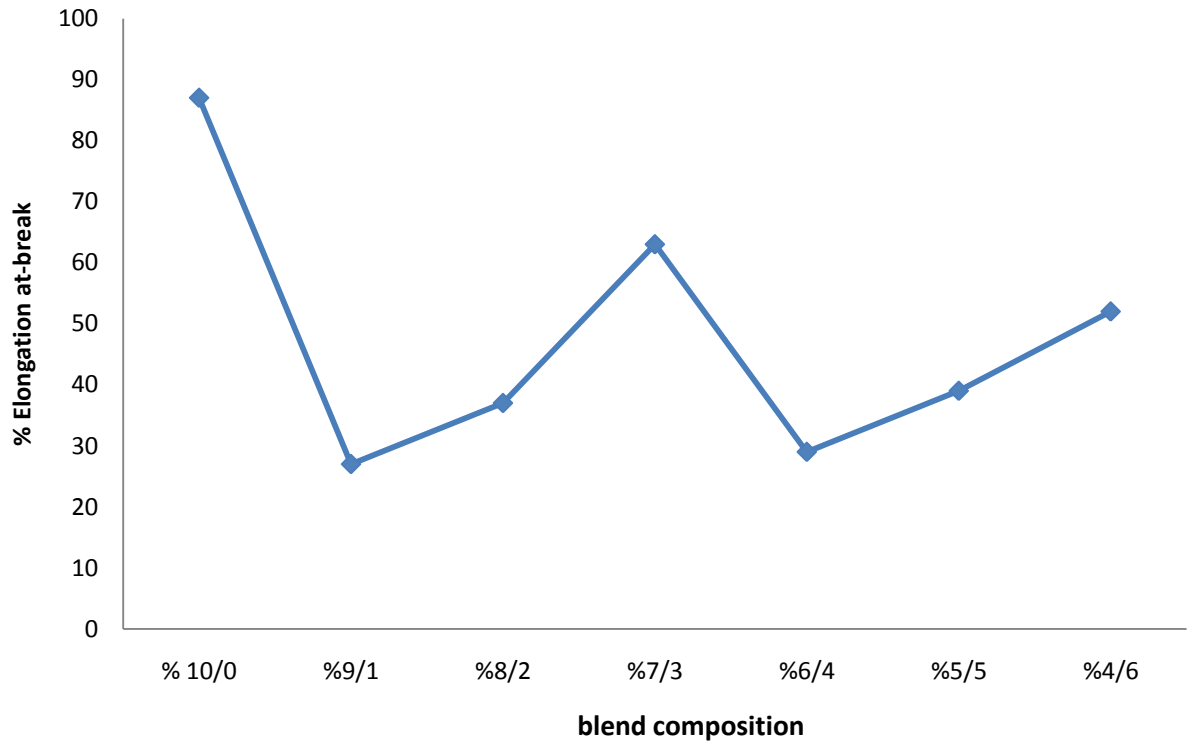



Fig. 4.4% Elongation at break against blend compositions

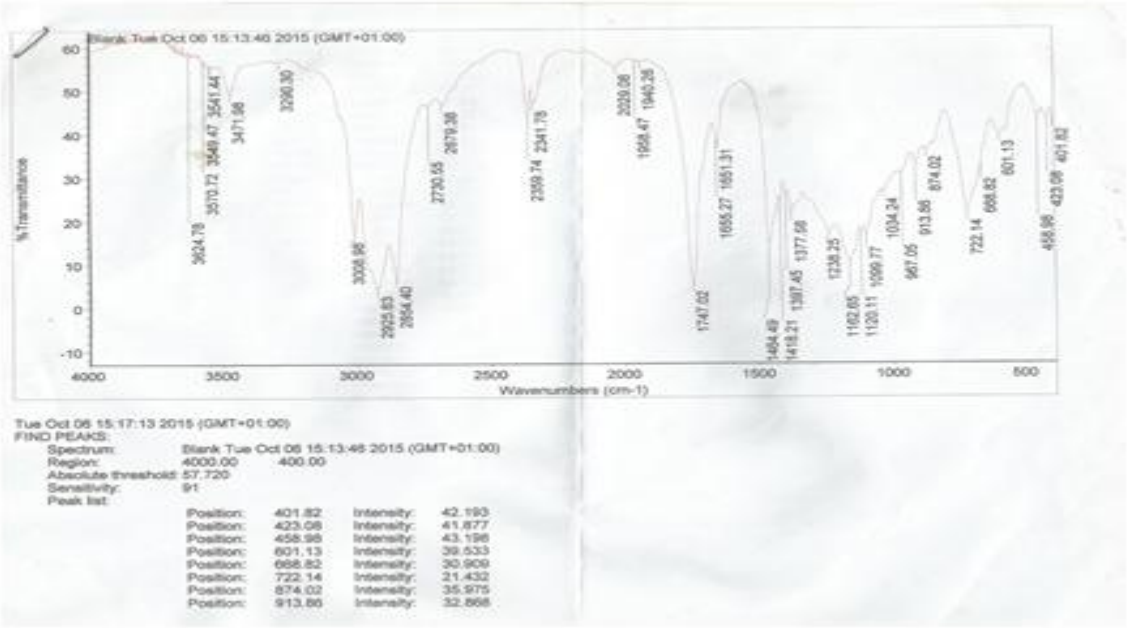
Table 4.3 Gives the FT-IR characteristic bands of soybean oil

| Wavenumber ($cm^{-1}$) | Assignment | Peak morphology | Reference |
|---|---|---|---|
| 722.14 | =C-H out of plane bending of cis-disubstituted double bond | Sharp peak | Oyerinde and Bello (2016) |
| 874.02 | =C-H out of plane bending of olefin | Lower sharp peak | Oyerinde and Bello (2016) |
| 913.86 | =C-H bending vibration of cis-di-substituted double bond | ,, | Guillen and Cabo (1997) |
| 1099.77 | C-O stretching of ester group | ,, | Guillen and Cabo (1997) |
| 1162.65 | C-C (=O)-O stretching vibration of | Sharp peak | Guillen and Cabo |

| | | | |
|---|---|---|---|
| | unsaturated ester group | | (1997) |
| 967.05 | =C-H out of plane bending of trans-di-substituted double bond | Lower sharp peak | Oyerinde and Bello (2016) |
| 1238.25 | C-C (=O)-O stretching vibration of saturated ester group | Sharp peak | Guillen and Cabo(1997) |
| 1418.21 | C-H rocking vibration cis-di-substituted olefin | Sharp peak | Oyerinde and Bello (2016) |

| | | | |
|---|---|---|---|
| 1655.27 | C=C stretching vibration of cis-double bond | Sharp peak | ,, |
| 1377.58 | C-H bending of alkane | Low sharp peak | ,, |
| 1397.45 | C-H rocking of alkane | Low sharp peak | ,, |
| 1747.02 | C=O stretching of the unsaturated fatty-acid group | Very sharp peak | ,, |
| 2925.63 | Asymmetric stretching of C-H (alkane group) | Very sharp peak | ,, |
| 2854.40 | Symmetric stretching of C-H (methylene) | Very sharp peak | ,, |
| 3008.98 | C-H stretching vibration of the cis-double bond | Very sharp peak | ,, |

| | | | | |
|---|---|---|---|---|
| 3479.98 | O-H stretching | | Sharp peak | Oyerinde and Bello (2016) |



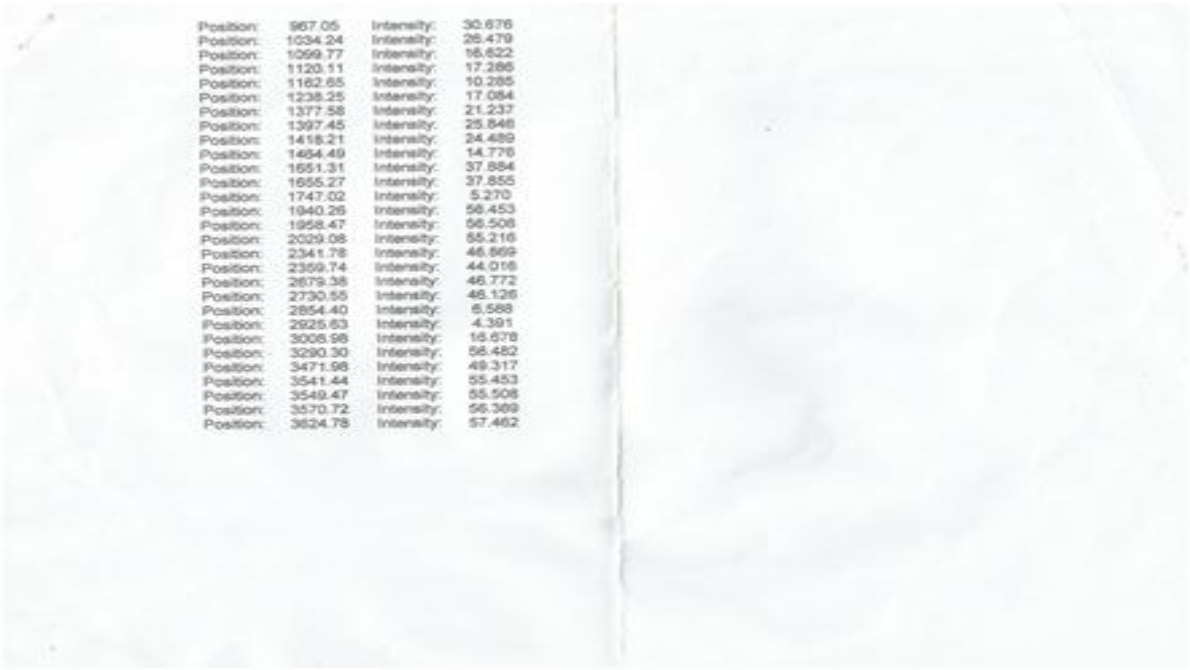
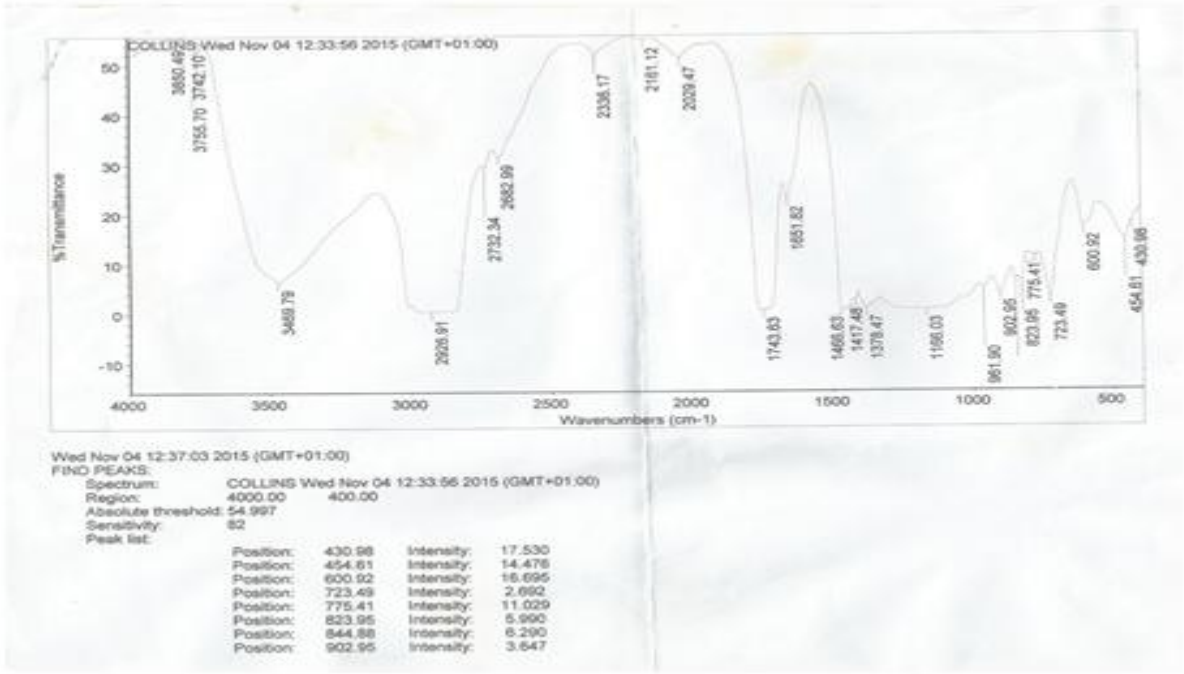



Fig. 4.5 FT-IR spectraof soybean oil

Table 4.4FT-IR characteristic bands of epoxidized soybean oil (ESO)

| Wavenumber ($cm^{-1}$) | Peak morphology | Assignment | References |
|---|---|---|---|
| 723.49 | Sharp peak | =C-H out of plane bending of cis-di, substituted double bond | Oyerinde and Bello (2016) |
| 775.41 | Lower sharp peak | C-O-C stretching of internal epoxy group | Bomstein (1958) |

| | | | |
|---|---|---|---|
| 823.95 | Lower sharp peak | C-O-C stretching of external oxirane ring | Bomstein (1958) |
| 844.88 | Overlapped | C-O-C stretching of internal oxirane ring | Bomstein (1958) |
| 902.95 | | C-O stretching of the oxirane ring | George *et al* (1991) |
| 1166.03 | | C-C (=O)-O stretching vibration of saturated ester group | Guillen and Cabo (1997) |
| 2926.91 | Lower broad peak | Asymmetric stretching of C-H (alkane group) | Oyerinde and Bello (2016) |
| 3469.79 | Sharp peak | O-H stretching | Oyerinde and Bello (2016) |



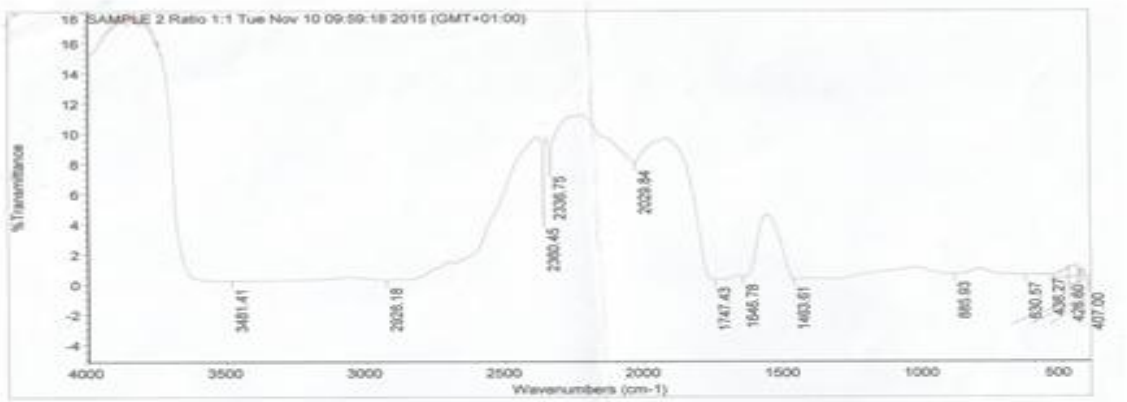

Wed Nov 04 12:37:03 2015 (GMT+01:00)
FIND PEAKS:
Spectrum: COLLINS Wed Nov 04 12:33:56 2015 (GMT+01:00)
Region: 4000.00 400.00
Absolute threshold: 54.997
Sensitivity: 82
Peak list:

| | | | |
|---|---|---|---|
| Position: | 430.98 | Intensity: | 17.530 |
| Position: | 454.61 | Intensity: | 14.476 |
| Position: | 600.92 | Intensity: | 16.695 |
| Position: | 723.49 | Intensity: | 2.692 |
| Position: | 775.41 | Intensity: | 11.029 |
| Position: | 823.95 | Intensity: | 5.990 |
| Position: | 844.88 | Intensity: | 6.290 |
| Position: | 902.95 | Intensity: | 3.647 |
| Position: | 961.90 | Intensity: | 4.774 |
| Position: | 1166.03 | Intensity: | 0.400 |
| Position: | 1378.47 | Intensity: | 0.641 |
| Position: | 1417.48 | Intensity: | 2.187 |
| Position: | 1466.63 | Intensity: | 0.449 |
| Position: | 1651.82 | Intensity: | 22.748 |
| Position: | 1743.63 | Intensity: | 0.371 |
| Position: | 2029.47 | Intensity: | 51.100 |
| Position: | 2161.12 | Intensity: | 54.881 |
| Position: | 2336.17 | Intensity: | 49.619 |
| Position: | 2682.99 | Intensity: | 31.387 |
| Position: | 2732.34 | Intensity: | 29.269 |
| Position: | 2926.91 | Intensity: | 0.315 |
| Position: | 3469.79 | Intensity: | 6.377 |
| Position: | 3742.10 | Intensity: | 53.979 |
| Position: | 3755.70 | Intensity: | 54.506 |
| Position: | 3850.49 | Intensity: | 54.911 |

Fig. 4.6FT-IR spectra of epoxidized soybean oil (ESO)

Table 4.5 gives the FT-IR characteristic bands of thermally cured soybean oil epoxy resin

| Wavenumber ($cm^{-1}$) | Peak morphology | Assignment | Reference |
|---|---|---|---|
| 2926.18 | Very broad peak, | Asymmetric C-H stretching of alkane | Oyerinde and Bello (2016) |
| 3481.41 | Very Broad peak, | O-H stretching | Oyerinde and Bello (2016) |




Tue Nov 10 10:01:24 2015 (GMT+01:00)
FIND PEAKS:

| | | | |
|---|---|---|---|
| Spectrum: | SAMPLE 2 Ratio 1:1 Tue Nov 10 09:59:18 2015 (GMT+01:00) | | |
| Region: | 4000.00 | 400.00 | |
| Absolute threshold: | 12.465 | | |
| Sensitivity: | 66 | | |
| Peak list: | | | |
| Position: | 407.00 | Intensity: | -0.173 |
| Position: | 426.60 | Intensity: | 0.639 |
| Position: | 436.27 | Intensity: | 0.766 |
| Position: | 442.56 | Intensity: | 0.877 |
| Position: | 477.85 | Intensity: | 1.001 |
| Position: | 529.76 | Intensity: | 0.542 |
| Position: | 630.57 | Intensity: | 0.531 |
| Position: | 885.93 | Intensity: | 0.599 |
| Position: | 1463.61 | Intensity: | 0.312 |
| Position: | 1646.78 | Intensity: | 0.462 |
| Position: | 1747.43 | Intensity: | 0.277 |
| Position: | 2029.84 | Intensity: | 8.052 |
| Position: | 2336.75 | Intensity: | 7.645 |
| Position: | 2360.45 | Intensity: | 9.414 |
| Position: | 2926.18 | Intensity: | 0.268 |
| Position: | 3481.41 | Intensity: | 0.218 |

Fig.4.7FT-IR spectra of thermally cured soybean oil epoxy resin

Table 4.6 Viscosity measurement of various blend ratios at $23^{O}C$

| %PS/ MESO | Conc. (g/L) $C_1V_1=C_2V_2$ | $T_i$ (seconds) | Relative viscosity $V_r = T_0/T_i$ | Specific viscosity $V_s = V_r - 1$ | Reduced viscosity $V_{red}=V_s/conc.$ |
|---|---|---|---|---|---|
| 5/5 | 0.01 | 185 | 1.83 | 0.83 | 83 |
| | 0.007 | 160 | 1.58 | 0.58 | 83 |
| | 0.005 | 150 | 1.49 | 0.49 | 98 |
| | 0.004 | 140 | 1.39 | 0.39 | 98 |
| 6/4 | 0.01 | 192 | 1.90 | 0.90 | 90 |
| | 0.007 | 170 | 1.68 | 0.68 | 97 |
| | 0.005 | 150 | 1.49 | 0.49 | 98 |
| | 0.004 | 141 | 1.40 | 0.40 | 100 |
| 7/3 | 0.01 | 195 | 1.93 | 0.93 | 93 |
| | 0.007 | 180 | 1.78 | 0.78 | 111 |
| | 0.005 | 170 | 1.68 | 0.68 | 136 |

| | | | | | |
|---|---|---|---|---|---|
| | 0.004 | 165 | 1.63 | 0.63 | 158 |
| 10/0 | 0.01 | 200 | 1.98 | 0.98 | 98 |
| | 0.007 | 171 | 1.69 | 0.69 | 99 |
| | 0.005 | 151 | 1.50 | 0.50 | 100 |
| | 0.004 | 141 | 1.40 | 0.40 | 100 |
| 0/10 | 0.01 | 102 | 1.01 | 0.01 | 1 |
| | 0.007 | 102 | 1.01 | 0.01 | 1.5 |
| | 0.005 | 102 | 1.01 | 0.01 | 2 |
| | 0.004 | 102 | 1.01 | 0.01 | 2.5 |

$T_0$ of the solvent (chloroform) used = 101 Seconds

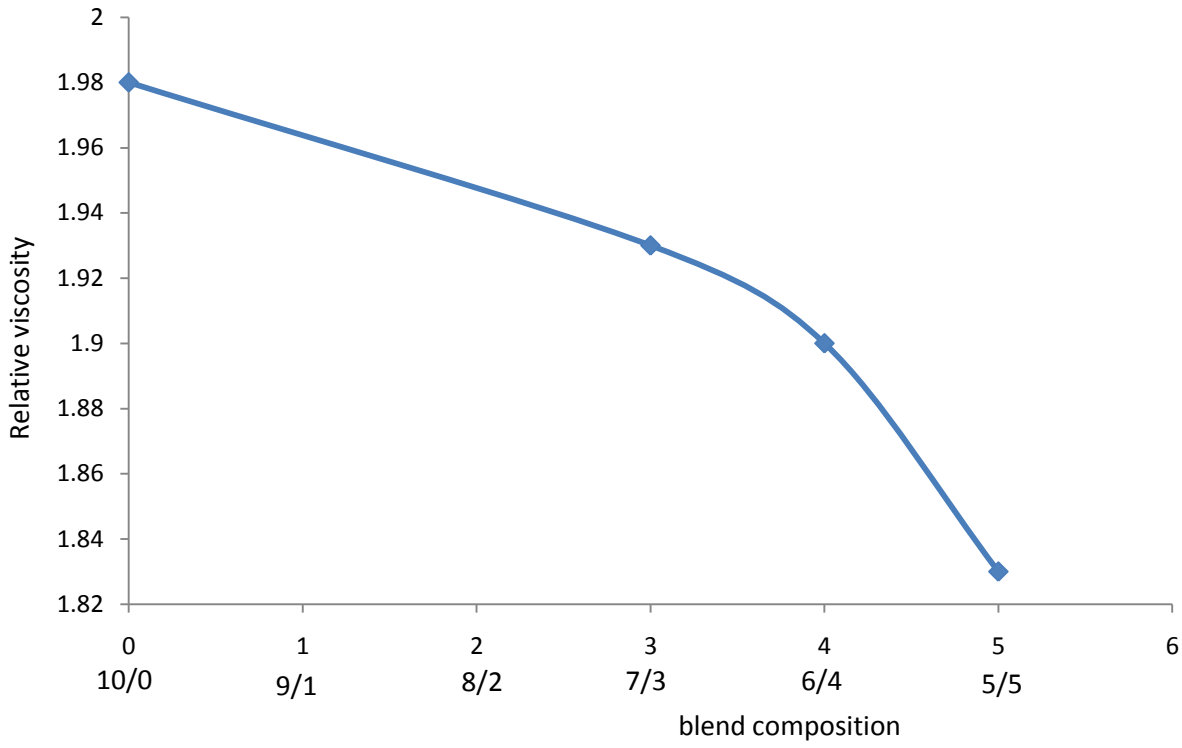



Fig. 4.8 Plot of relative viscosity against blend compositions

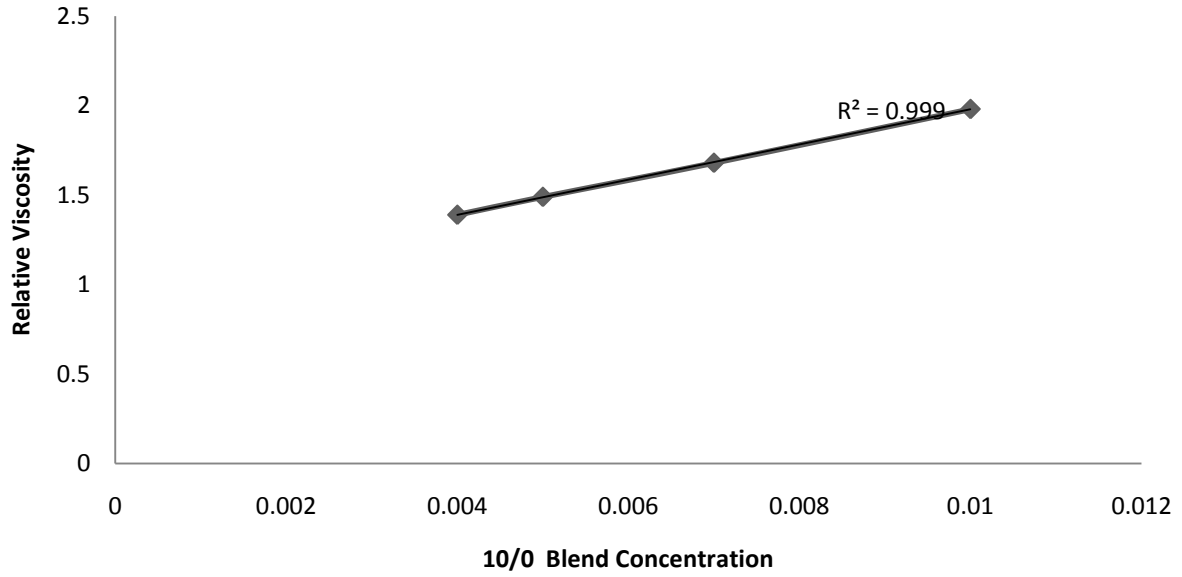


Fig. 4.9 Plot of relative viscosity of 10/0 PS/MESO blend against its concentration.

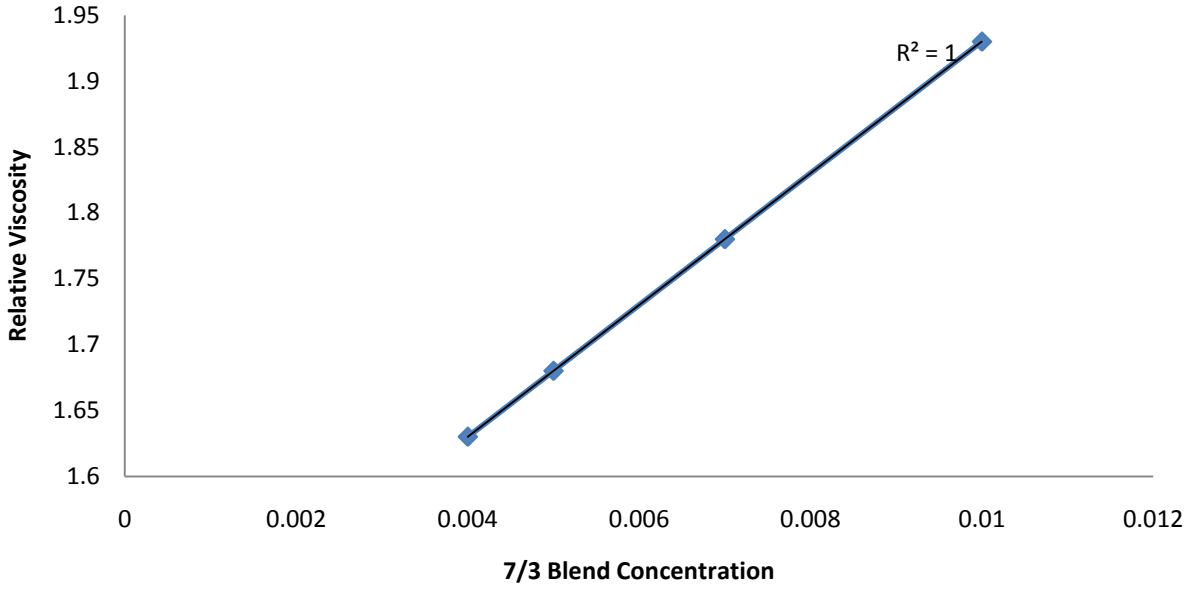



Fig. 4.10 Plot of relative viscosity of 7/3 PS/MESO blend against its concentration.

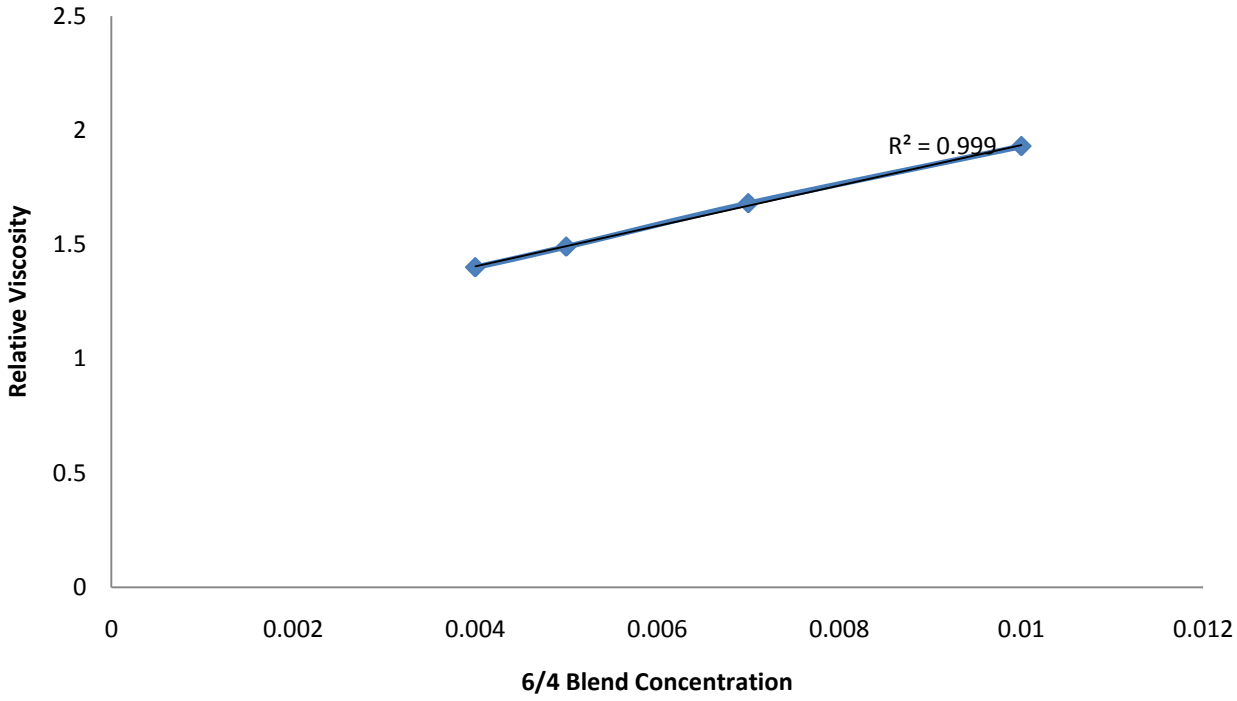


Fig. 4.11 Plot of relative viscosity of 6/4 PS/MESO blend against its concentration

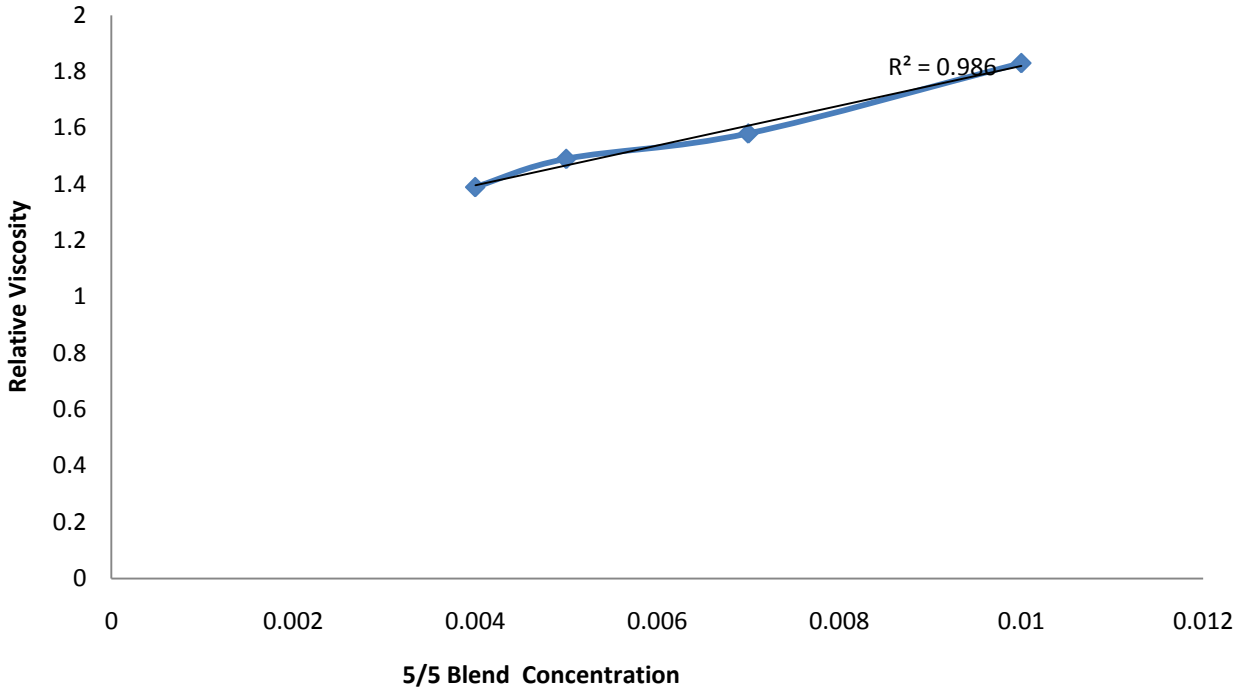



Fig. 4.12 Plot of relative viscosity of 5/5 PS/MESO blend against its concentration

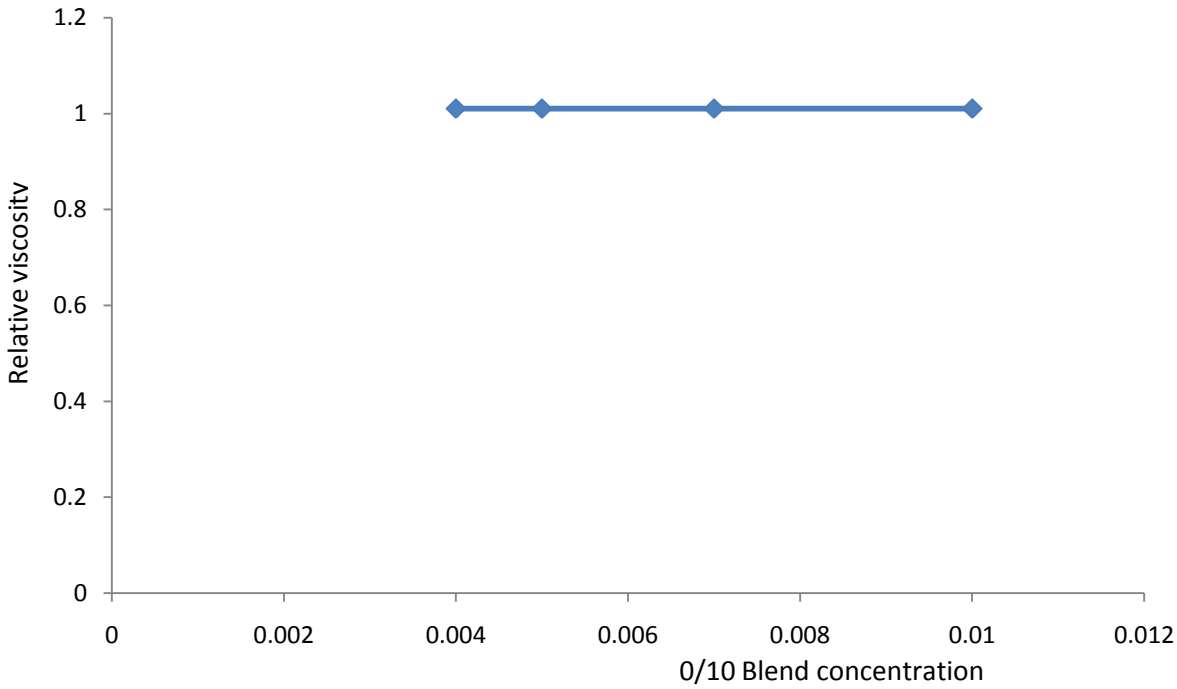



Fig. 4.13 Plot of relative viscosity of 0/10 blend against its concentration

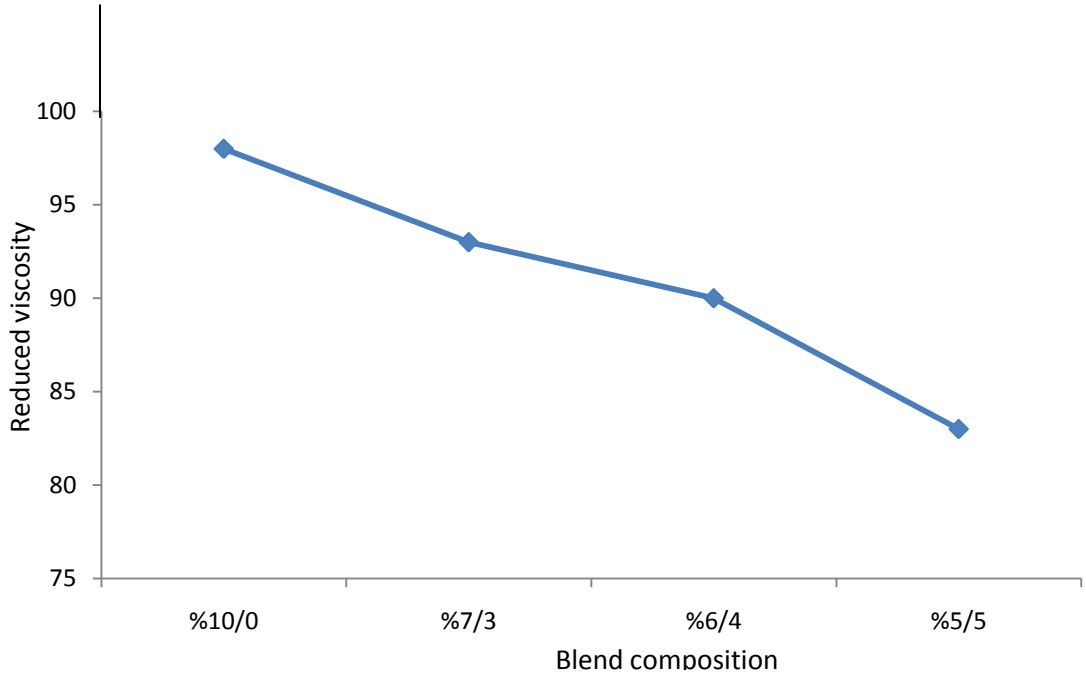



Fig. 4.14 Plot of reduced viscosity against blend compositions

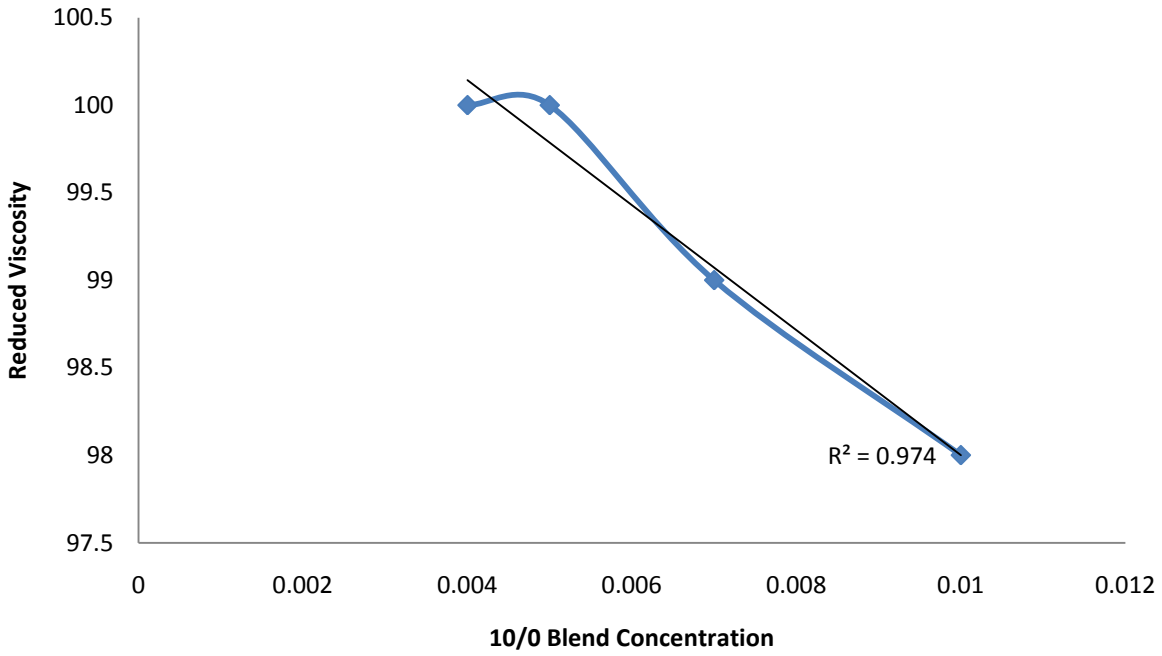



Fig. 4.15 Plot of reduced viscosity 10/0 blend composition against its concentration

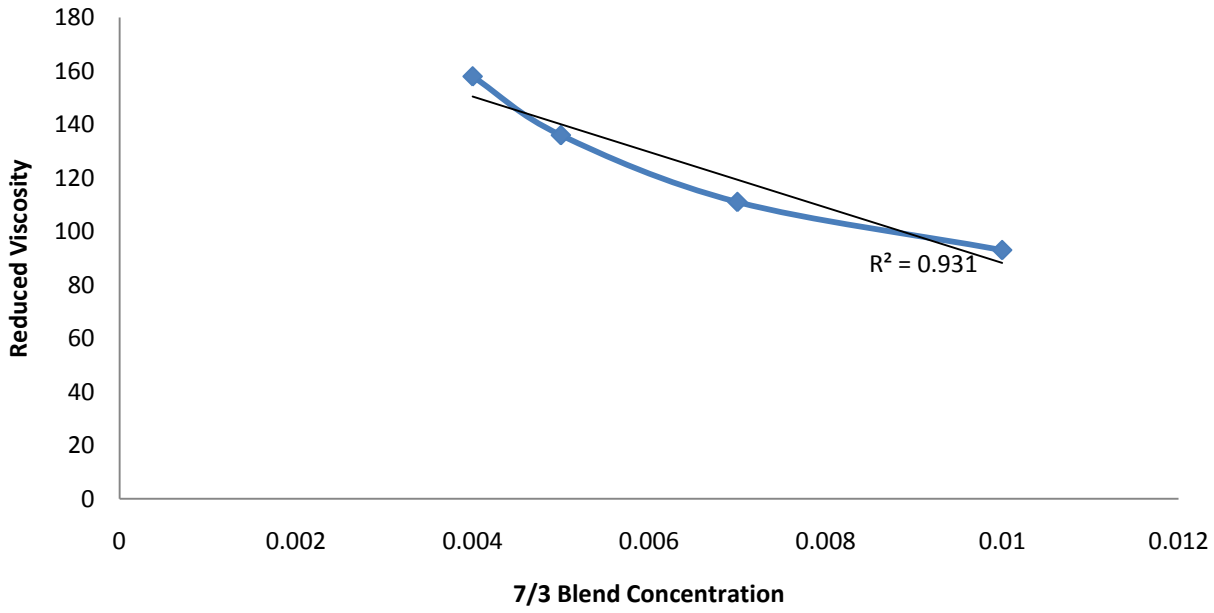



Fig. 4.16 Plot of reduced viscosity of 7/3 blend composition against its concentration

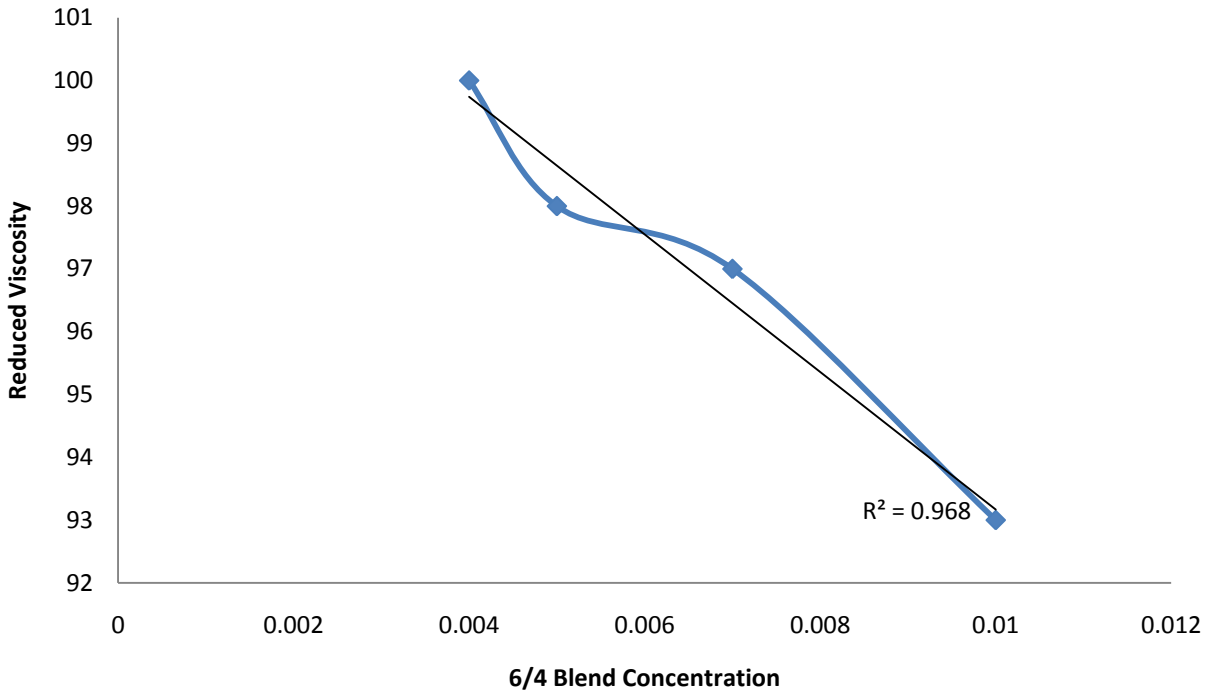



Fig. 4.17 Plot of reduced viscosity of 6/4 blend composition against its concentration

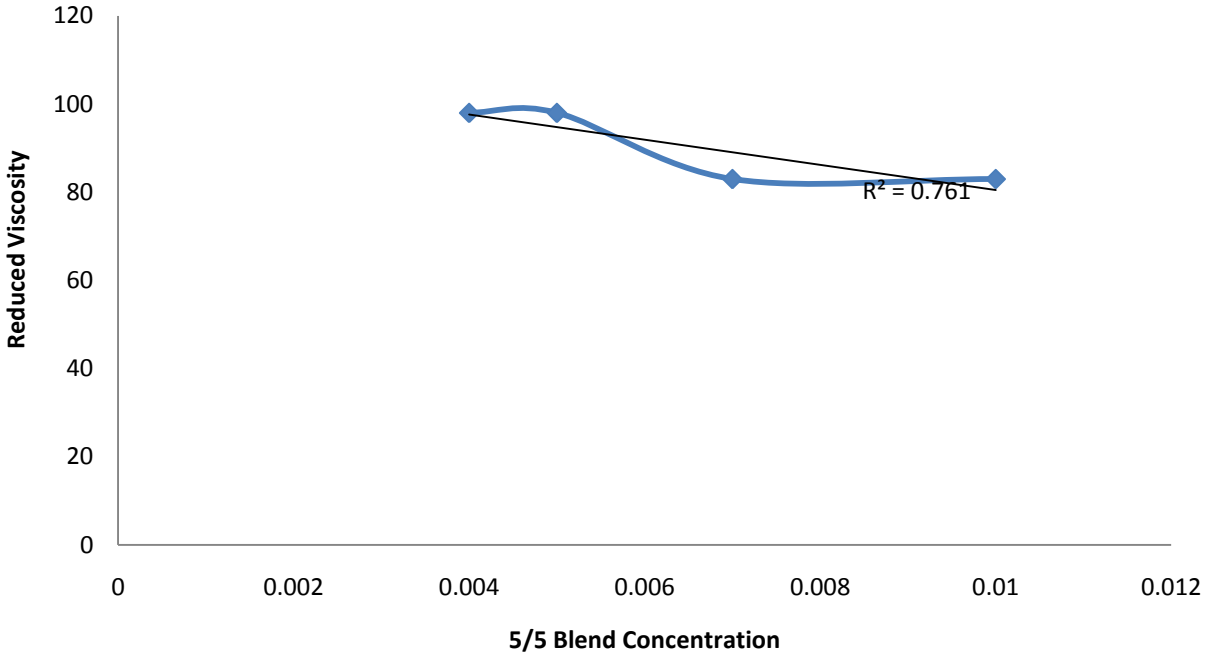



Fig. 4.18 Plot of reduced viscosity of 5/5 blend composition against its concentration

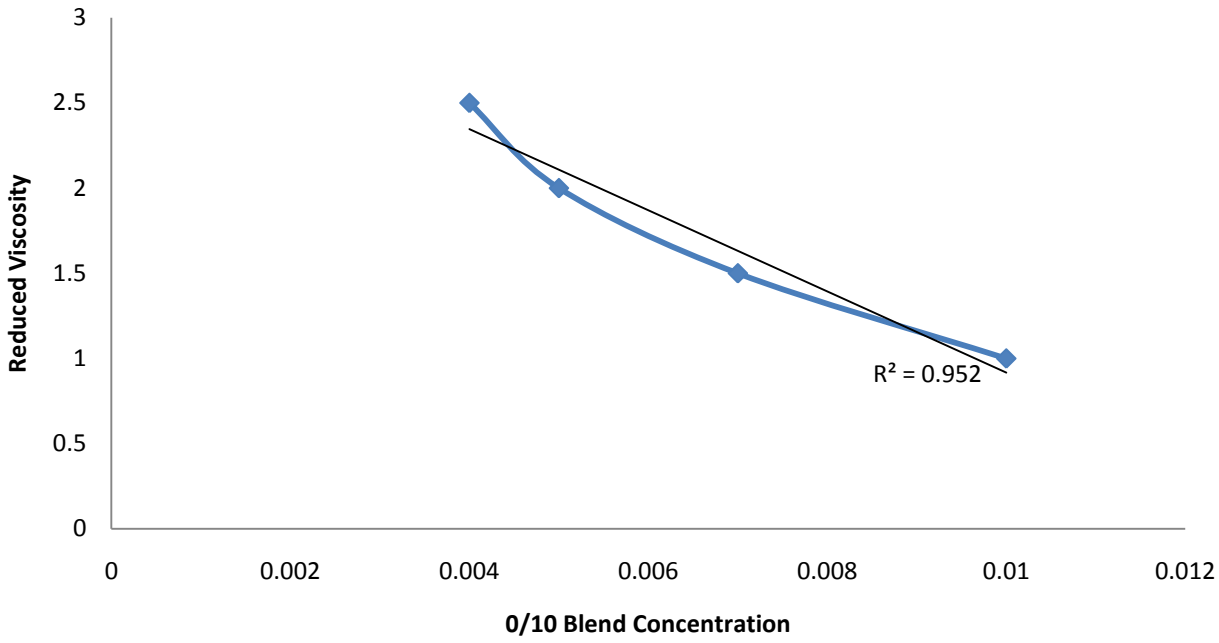



Fig. 4.19 Plot of reduced viscosity of 0/10 blend composition against its concentration

Table 4.7Table of $R^2$ values vs blend's compositions

| PS/MESO | % $R^2$forRelative viscosity | % $R^2$forReduced viscosity |
|---|---|---|
| 5/5 | 98.6 | 76.2 |
| 6/4 | 99.9 | 96.8 |
| 7/3 | 1 | 93.1 |
| 10/0 | 99.9 | 97.4 |
| 0/10 | NA | 95.2 |

Extrapolated from the plot of both relative andreduced viscosity of the blend composition against blend concentrations

# CHAPTER FIVE

# DISCUSSION

## 5.1 THE IODINE NUMBER AND EPOXY CONTENTS

The result gave the percentage of oxirane-oxygen content (i.e the three membered epoxy ring) to be 9.77%.Wang and Schmman, (2012) noted in a review that "an epoxidized vegetable oil (EVO) of low oxirane-oxygen values are either not reactive or impart waxy, non-curing properties to the resin system". They reported 6.9 %, and 9.3 % as oxirane-oxygen content of ESO and ELO respectively. Kouroosh*et al*(2012) reported 6.3% as oxirane-oxygen content of ESO. Table4.1 also gave the number of carbon-carbon double bonds (i.e, the Iodine number) present in soybean oil sample obtained from Grand Company Jos, to be 149.8.Tayde*et al* (2012) noted 120-150 $I_2$g/100g as the range of iodine number in soybean oil sample.

## 5.2 MECHANICAL PROPERTIES OF THE BLEND

Xu *et al* (2004)reported that ESO can be cross-linked into thermosetting polymers by various curing agents. They also noted that "only those oils of poly-unsaturated fatty-acid content especially soybean or linseed oils that can produce dense oxirane functional resins are capable to produce satisfactory properties. Tanrattanakul and Saithai (2009) found that the mechanical properties of the cured ESO can be improved with the addition of nano-reinforcement or fiber reinforcement according to Liu *et al* (2006).Therefore, compatible polymer blends form single-phase systems and have a single property like the glass transition temperature-the value of which is generally the weighted average of the components of the blend. At certain composition, some compatible polymer blends exhibit strong intermolecular attraction and hence have a high level of thermodynamic compatibility. This often results in properties superior to those of the

individual components alone. It is known that the mechanical properties of polymer blends depend on the intermolecular forces, chain stiffness, steric factor, molecular symmetry of the individual polymers used to prepare the blend (Mudigoudra *et al*, 2012). In general, the introduction of ring system into the main chain can provide a better structural mechanism for toughening polymers than chain stiffening by bulky side group.

5.2.1Tensile Strength `

As defined in section 2.9.8, the ability to sustain dead load or the stress at which the specimen ruptures. Elgozali and Hassan (2008) have observed that the tensile strength decreases with increasing plasticizer content for the group of sample free of filler. The tensile strength of the polystyrene- modified epoxy resin of soybean oil (PS / MESO) blend follows a sinusoidal wave pattern with increasing composition of MESO in blend. The wave pattern seen in the Fig. 4.2 shows crest and trough at even and prime number composition of the blend respectively. The pattern continued till the polystyrene matrix can no longer support the dispersed MESO at 4/6 PS/MESO blendcomposition which showed a discontinuity of the wave pattern. 6/4 PS/MESO blend gave the highest crest (the maximum displacement value-4.3 x $10^5$ $NM^{-2}$).

5.2.2. Young's Modulus of Elasticity

Young's modulus is defined as the ability to carry stress without changing dimension. It is a measure of stiffness of the material. Fig. 4.3 gives the trend of Young's modulus of all test samples. It's observed that the Young's modulus increases with increasing the composition of the dispersed phase (MESO) in the polymer matrix (polystyrene) at some blend compositions such as 9/1, 8/2, 6/4 and 5/5 PS/MESO blends respectively as compared with the 10/0 PS/MESO blend in Table 4.2, where as blends such as 7/3 and 4/6 PS/MESO shown deviation. The

deviation can be attributed to incompatibility at certain compositions. The 6/4 PS/MESO blend has the highest value of Young's modulus (approx. 1.5 x $10^6$ $NM^{-2}$).

5.2.3. Elongation-At-Break

Elongation at break may be viewed as a measure of deformation or plasticization. Fig. 4.4, shows that the percentage elongation-at-break of polystyrene decreases with increasing the content of thermally modified epoxy resin of soybean oil in the blends. Though, regular pattern of reduction in percentage elongation was not obtained due to strain rate, random distribution of molecules of the dispersed phase in the polymer matrix, among other factors. The blends with minimum % elongation at break are 9/1 and 6/4 PS/MESO blends with 27% and 29% respectively.The result indicates non-plasticizing effects of MESO on polystyrene polymer.

5.3.FT-IR CHARACTERISTIC BANDS' COMPARISON OF SPECTRA TABLES 4.3, 4.4, AND 4.5

Changes occur at positions (874.02, 913.86, 1034.24, 1099.77, 1238.25, 3008.98, 1397.45, and 1655.27)$cm^{-1}$. These positions are present in fig. 4.5., but absent in Fig. 4.6, and 4.7.

Changes occur at positions (775.41, 823.95, 844.88, 902.95)$cm^{-1}$. These positions are present in Fig. 4.6., but absent in Fig. 4.5., and 4.7, The appearance of these characteristic bands at these positions especially 775.41, 844.88 and 902.95 $cm^{-1}$ in the ESO spectral table 4.4, with the disappearance of the characteristic bands at position 913.86 and 3008.95$cm^{-1}$ in the soybean oil spectral Table 4.3, confirmed the conversion of double bonds in the mixed free fathy-acids of soybean oil to epoxy ring, Wang and Schmman, ( 2012).

Changes occur at positions (885.93, 1646.78, 2360.45)$cm^{-1}$. These characteristic bands' positions are present in fig. 4.7., but absent in fig. 4.5., and 4.6.

Changes occur at position (1377.58, 1418.21, 1651.31)$cm^{-1}$. These positions are present in Fig. 4.5., and 4.6., but absent in 4.7.

Changes do not occur at characteristic bands' positions (1747.43, 2926.18, and 3481.41)$cm^{-1}$. These positions are present in fig. 4.5., 4.6., and 4.7 respectively

Changes occur in position 2336.17$cm^{-1}$. This characteristic band' position is present in fig. 4.6., and 4.7.

## 5.4. VISCOSITY MEASUREMENTS

Mamza and Folaranmi (1996) and Kulshreshta*et al* (1988) have observed that the plot of the relative viscosity of the blend solution against composition is linear when the components are completely miscible or compatible, and non-linear or S-shaped when blends are incompatible indicating two phase formation with reversal of phases at intermediate composition.

### 5.4.1. Relative Viscosity

The plot of relative viscosity of blends against its composition shows a negative graph. In all the various blend compositions, the relative viscosity is less than 2.0 Fig. 4.8 shows a reduction in relative viscosity with increasing the content of thermally cured epoxy resin of soybean oil (MESO) in the polystyrene matrix. A linear plot is observed. The linearity of the plot affirmed the miscibility/ compatibility of the various PS/MESO blend compositions in chloroform (Ebewele, 2000k). Figs. 4.9—4.13 show positive graphs. As indicated in section 2.6, the viscosity of dissolved polymer solution relative to that of pure solvent increases even at low

concentration. The plots indicate increase in relative viscosity as the concentration of the blends increases. Blend 7/3 PS/MESO gives a perfect linear graph with $R^2$ of 1 (see table 4.7), though intercepted on negative y-axis of the plot. Whereas, in blend 0/10 PS/MESO, the increase in concentration does not affect its relative viscosity at various concentrations. Thus, its $R^2$ value is not available (NA).The $R^2$ value of 6/4 PS/MESO blend gives an additive value between 10/0 and 0/10 PS/MESO blends, indicating additive blend.

5.4.2. Reduced Viscosity

The plot of reduced viscosity of the blends against its concentration/composition can also be use to predict miscibility/compatibility like relative viscosity. In most cases, the plots assumed linearity until it reaches an infinitesimal concentration, i.e where decrease in concentration of the blend does not significantly affect its reduced viscosity. The plot in Fig. 4.14, is negative and linear (i.e, decreasing reduced viscosity on increasing the content of thermally cured soybean epoxy resin in the polystyrene matrix) confirming miscibility in chloroform. However, unlike the plot of relative viscosity of the blends against its concentration, the plot of reduced viscosity of the blend at different concentration shows a negative graph. That is, the reduced viscosity decreases with increasing concentration. Fig. 4.15—4.19, give the plot of various blend's compositions at different concentration.Fig. 4.16 and 4.18, give a non-synergistic curve but not S-shape (see fig.2.6), where as, fig. 4.17, gives the additive plot (linear) with reference to undiluted compositions of 10/0 and 0/10 PS/MESO blends in fig. 4.15, and fig. 4.19, respectively. The $R^2$ value of 6/4 PS/MESO blend indicates an additive value between 0/10 and 10/0 blends.Thus, the 6/4 PS/MESO blend showed a Newtonian behavior (i.e, fluid viscosity is

independent of strain rate) at certain point, indicating strong molecular interaction since the fluid viscosity is due to molecular interaction (Ebewele, 2000L).For non-Newtonian fluid, viscosity is dependent on the strain rate. In physical terms, non-Newtonian behavior means, that as molecules pass each other, their size, shape and cohesiveness determined how much force is required to maintain the movement. When the strain rate is changed, molecular alignment (interaction) may change, also as well as the force required to maintain motion.

# CHAPTER SIX

# SUMMARY,CONCLUSION AND RECOMMENDATIONS

## 6.1 SUMMARY

### Soybean oil characterisation

The iodine number (149.8) revealed that soybean oil has a high number of carbon-carbon double bonds. The FT-IR spectroscopic data revealed the characteristic bands of cis-di-substituted olefinic bonds.

### Synthesis and characterisation of ESO/MESO

Stoichiometric molar ratios of 2:1: 3 soybean oil, acetic acid and hydrogen peroxiderespectively were charged in a reactor under reflux for a reaction time of 5hrs. at $60^{O}$Cyielded a high content of oxirane-oxygen. FT-IR spectroscopic data revealed the appearance of internal and external oxirane – oxygen characteristic bands. Temperature elevation at $75^{O}$C caused gelation. FT-IR study of the gel revealed a dominant characteristic band of hydroxyl groups.

### Solution blending of polystyrene and MESO

Solution blending of polystyrene and MESO revealed the miscibility of both components in chloro-benzene at room temperature.

Mechanical properties of blends

Tensile strength and Young's modulus measurements revealed a higher (an improved) value at 6/4 PS/MESO composition, respectively. The percentage elongation-at-break revealed non-plasticizing effect of thermally cured epoxy resin of soybean oil (MESO) on polystyrene (PS) matrix.

Viscosity measurement of the blend

Relative viscosity studies revealed that thermally cured epoxy resin of soybean oil is compatible with polystyrene in chloroform. Reduced viscosity studies also identified the degree of compatibility of the blends and indicated that 6/4 PS/MESO blend curve was additive as reflected in the $R^2$ value of the plot.

## 6.2 CONCLUSION

Successes have been achieved on the set objectives of this study. In this research, epoxidation of soybean oil via conventional method gave a higher value (9.77%) of oxirane-oxygen content. The FT-IR characteristic bands of oxirane-oxygen groups occurred at $824cm^{-1}$, $845cm^{-1}$, and $903cm^{-1}$.

However, epoxidation of soybean oil by the same method but at a higher temperature ($85^{O}C$) destroyed the oxirane ring (i.e, oxirane-oxygen groups) with resultant ring opening and attendant hydroxyl (OH) groups formation as confirmed in the FT-IR characteristic bands in Fig. 4.7. The thermally cured(modified)epoxidized soybean oil (MESO) was blended with the polystyrene at different proportions. The mechanical tests showed a random pattern with increasing the amount of polystyrene in the blend. The blend of 6/4 PS/MESO composition showed an increased tensile

stress and Young's modulus with very low elongation-at-break. Further compatibility assessment of 6/4 PS/MESO blend via viscosity measurement gives additive shaped blend type. The improved mechanical behavior at 6/4 PS/MESO composition, may also be attributed to toughing or reinforcing effect of polar hydroxyl groups.Thus, this composition deviated from the expected plasticizing effect (i.e increasing elongation-at-break and lowering tensile strength), and exerted a reinforcing effect on the polystyrene. Thus, thermally cured ESO at certain composition can actas a fibre reinforced plastic.

## 6.3 RECOMMENDATIONS

This research encourages more interest in the diversification of soybean oil and thus, put forward the following recommendations;

(i). Effort should be made to commercialized the synthesis of epoxidized soybean oil in Nigeria in order to reduce forex demand for industrial chemicals since ESO is a precursor for many industrial chemicals

(ii). More research works on thermal curing of epoxidized soybean oil should be encouraged.

## 6.4 CONTRIBUTIONS TO KNOWLEDGE

(i) This study encourages the production of soybean oil epoxyl resin with reference to higher value (9.77%) of oxirane oxygen content.

(ii)The study also hinted on the use of heat to effect curing of epoxyl resin of soybean oil.

(iii) The study also hinted on the use of thermally cured epoxyl resin of soybean oil as a reinforcement to plastic materials with reference to higher values of tensile strength ($4.3 \times 10^5$ $NM^{-2}$) and Young's modulus ($1.5 \times 10^6$ $NM^{-2}$)at 6/4 PS/MESO blend composition respectively.

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Plate 1:Soybean oil sample



Plate 2:Set-up for epoxidation of soybean oil



Set-up for epoxidation of soybean oil

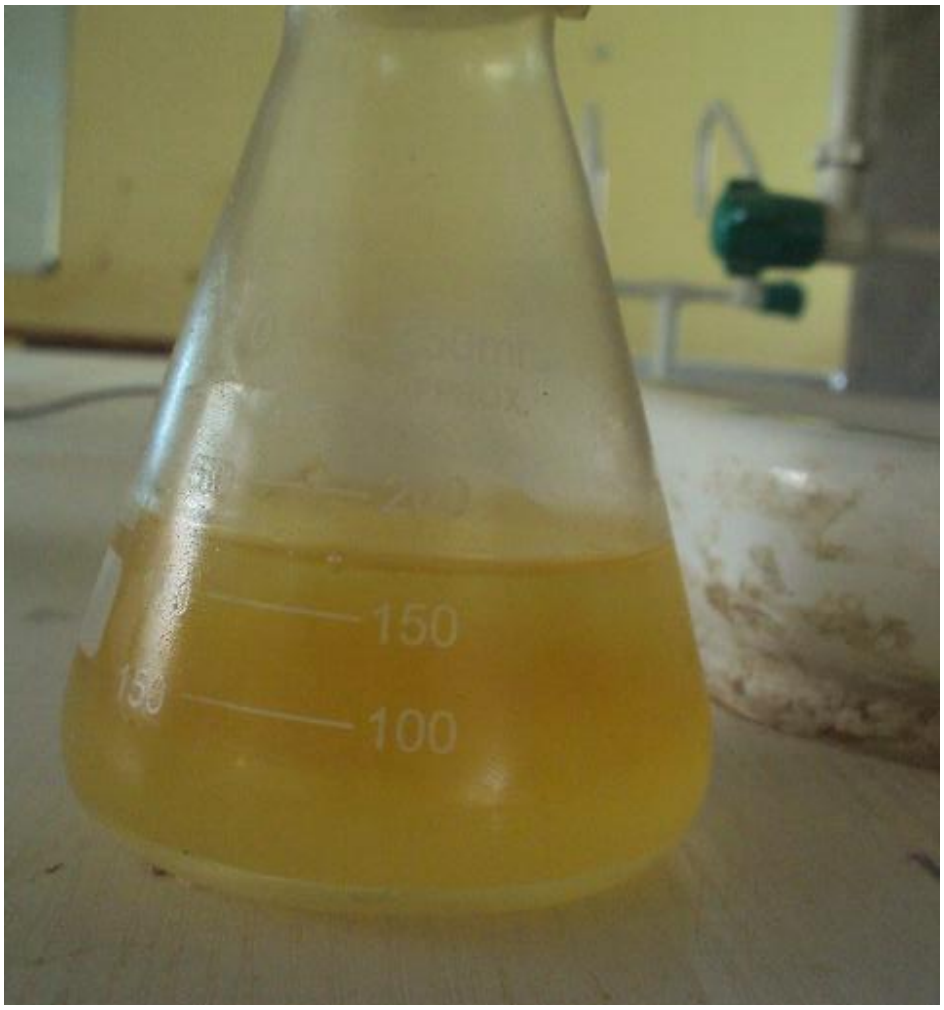



Plate 3: Synthesized epoxy resin of soybean oil




Plate 4:FT-IR spectrophotometer



Plate 5:Thermally cured epoxidized soybean oil resin (MESO)



Plate 6:Mode for casting of blends

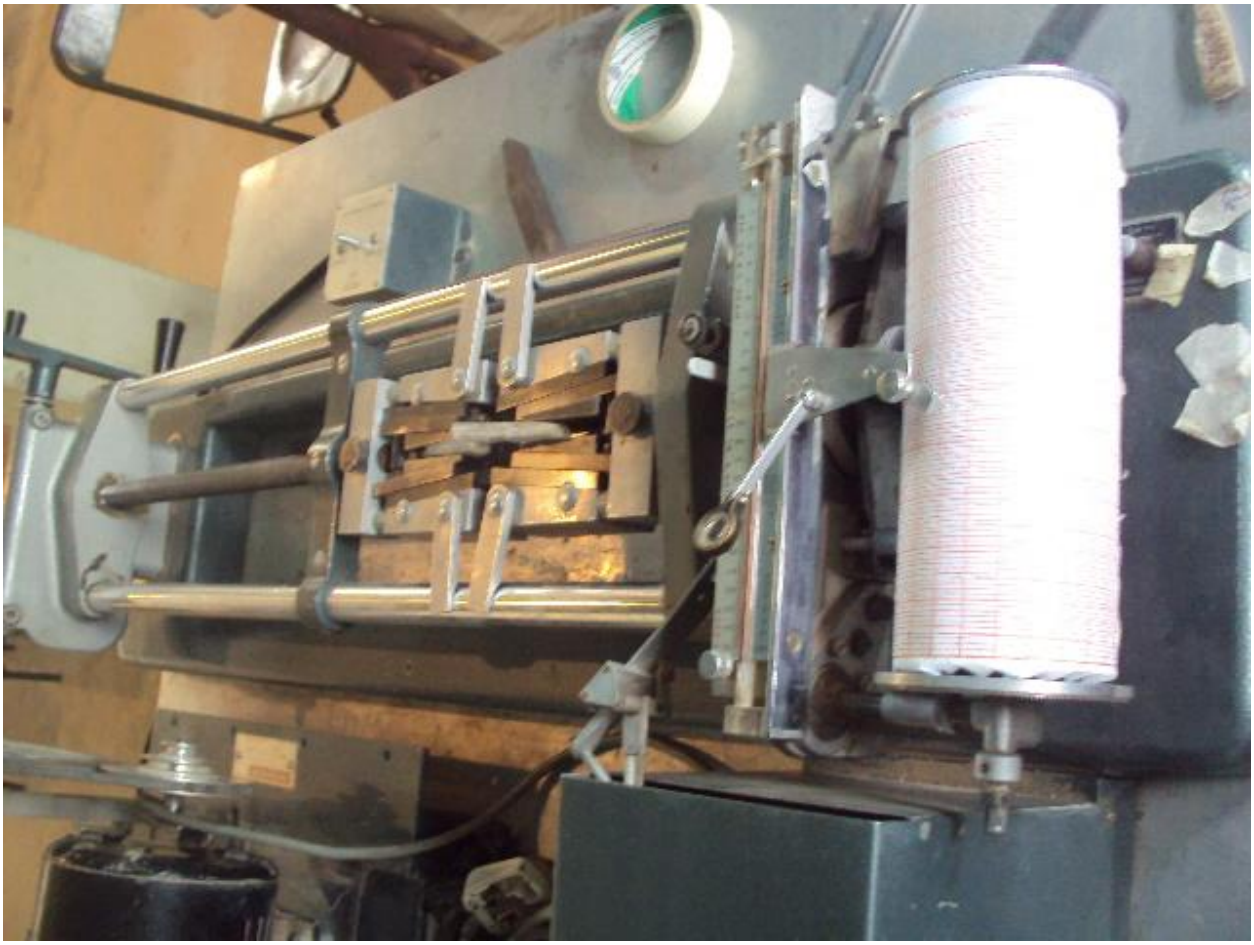


Plate 7:Tensiometer



Plate 8:Viscosity measurement set-up

**Appendix 1: (Preparation of 0.5 M molar solution of $H_2SO_4$)**

Stock solution information

Specific gravity = 1.83 g/mL

Molar mass = 98.08 g/mol.

Thus,

Molarity of stock solution = specific gravity/ molar mass

$$= 1.83/98.08 = 0.0186 \times 10^3 M$$

It means that 1L of $H_2SO_4$ contains 18.6 Moles of solute, then 0.5 moles will be equivalent to = 0.5/18.6 = 26.8 mL of $H_2SO_4$

Therefore, 26.8 mL of $H_2SO_4$ is equivalent to 0.5M $H_2SO_4$

**Appendix 2: (Preparation of 0.1 mol/L $Na_2S_2O_3$for iodine number determination)**

Molar mass = 158 g/mol

Thus,

Moles = mass in gram / molar mass

Therefore, mass in gram = 0.1 x 158 = 15.8 g/L

It means that 15.8 g in 1L of distilled water contains 0.1 moles of solute.

**Appendix 3: (Calculation for iodine value determination)**

Blank titration

$1^{st}$titre value = 51.5

$2^{nd}$titre value = 51.7

Average blank titre value = 51.6 mL

Sample titration

$1^{st}$titre value = 48.9

$2^{nd}$titre value = 49.2

Average sample titre value = 49.05 mL

Iodine value = ((blank – sample)mL x 0.1 x 1.269 x 100))/ 0.216

IV = 149.8

**Appendix 4: (Calculation of stoichiometric equation for epoxidation)**

Mole of C = C present in 100g of soybean oil sample= Iodine number/ iodine molar mass

Mole of C = C: 149.8/254 = 0.59

Ratio of $CH_3COOH$ = (Mole of C = C) x 0.5= 0.59 x 0.5= 0.295

Ratio of $H_2O_2$ = (Mole of C = C) x 1.5 = 0.59 x 1.5 = 0.885

Thus, stoichiometric representation,

C = C in soybean oil = 0.59/0.295 = 2

$CH_3COOH$ = 0.295/0.295 = 1

$H_2O_2$ = 0.885/0.295 = 3

Derivation of actual mass (g) of reagents for epoxidation

Theoretical Mass of soybean oil = 100g

$CH_3COOH$ = molar ratio x molar mass = 0.295 x 60 = 17.71g

$H_2O_2$ = molar ratio x molar mass = 0.885 x 34/40% = 100.3g

Volumetric conversion

$CH_3COOH$ = actual mass /density = 17.71g / 1.05g/mL = 16.87mL

$H_2O_2$ = ,, =100.3g / 1.12g/mL = 89.55mL

Soybean oil = ,, = 100g / 0.985 g/mL = 101.52mL

Volume of $H_2SO_4$ = 2% of total volume of $H_2O_2$ and $H_2SO_4$ = 2.13mL

**Appendix 5: (Calculation of % oxirane – oxygen content of ESO)**

Standardization of HBr

1st titre value = 11.3

2nd titre value = 11.1

Average titre value = 11.2 mL

Normality of HBr = mass of acid phthalate/ 0.2042 x mL HBr

= 0.42/0.2042 x 11.2 = 0.18 N

Sample titration

Rough titre value = 18.8

1st titre value = 19.1

2nd titre value = 18.1

Average sample titre value = 18.66 mL

Thus,

% oxirane-oxygen content = mL HBr x normality of HBr x 1.6 / sample mass

= 18.66 x 0.18 x 1.6/ 0.55

= 9.77%

**Appendix 6: (Tensiometer measurement of the blends)**

| Sample PS/MESO | Width W (mm) | Thickness T (mm) | Gauge L length (mm) | ΔL (mm) | Load (N) | Area TxW(mm)$^2$ |
|---|---|---|---|---|---|---|
| 10/0 | 8.4 | 1.5 | 40 | 32.4 | 48 | 12.6 |
| 9/1 | 8.8 | 2.2 | 45 | 12 | 42 | 19.36 |
| 8/2 | 9.0 | 1.1 | 49 | 18 | 30 | 9.9 |
| 7/3 | 7.1 | 2.1 | 53 | 33.6 | 30 | 14.91 |
| 6/4 | 7.0 | 1.3 | 50 | 14.4 | 39 | 9.1 |
| 5/5 | 7.8 | 1.3 | 51.8 | 20.4 | 24 | 10.14 |
| 4/6 | 8.2 | 1.8 | 51 | 26.4 | 21 | 14.76 |

ΔL is extrapolated from the graph in x-axis where;

1 complete revolution = 21 units

1 unit = 1.2 mm

Force applied (load) is extrapolated from the graph in y-axis where;

Total force of the tensiometer = 300N

Unit of graph = 30 N

Mini unit = 3N

**Appendix 7: (Pressure Conversion)**

$1NM^{-2} = 10^{-5}$ MPa (mega Pascal)

$1NM^{-2} = 1.45 \times 10^{-4}$ Psi ( pounds per square inch)

**Appendix 8: (Viscometric dilution formula)**

$C_1V_1 = C_2V_2$

$C_1 = 0.01$ when $V_1 = 10$

$C_2 = 0.007$ when $V_2 = 15$

$C_3 = 0.005$ when $V_3 = 20$

$C_4 = 0.004$ when $V_4 = 25$

$C_5 = 0.003$ when $V_5 = 30$