CHAPTER 2
CHAPTER 2

EXPERIMENTAL SECTION

The details of experimental procedures carried out throughout the work are described in this chapter. The method adopted for the preparation of various polymers, determination of physiochemical properties such as acid value, iodine value, saponification value, hydroxyl value, specific gravity and intrinsic viscosity, characterization of polymers etc. are discussed in this section.

2.1 Synthesis of polymers

2.1.1 Materials used

* Linseed oil used is refined linseed oil marketed by Camlin Ink India Ltd purchased from local market at Trivandrum.
* Sesame oil is commercial grade obtained from local market.
* The chemicals Cyclohexane dicarboxylic anhydride (Sigma–Aldrich), Triethylene glycol dimethyl acrylate (TEGMA) (Sigma–Aldrich), Glycerol, Methyl acrylate, Methyl methacrylate, Vinyl acetate, N-vinyl-2-pyrrolidone, Benzoyl peroxide, N,N – dimethyl aniline, NaOH, anhydrous methanol were used without purification.
* Fillers such as sisal fiber, coconut fiber, wood flour and wheat flour were commercial grade obtained from local market.

2.1.2 Synthesis of polymers from linseed oil

2.1.2.1 Preparation of alkyd resin
Glycerol was heated about 220 - 230ºC for 2 hours at nitrogen atmosphere to remove trace amount of water. Linseed oil and glycerol in the ratio 2:1 was taken in a three necked flask. (Linseed oil is added in five steps in 1 hour interval) A commercial soap or NaOH (1% weight) was added and the solution was heated for 5.5 hours at 220 – 230ºC. The completion of reaction was confirmed by the formation of a clear solution in anhydrous methanol [157]. The reaction flask was cooled to room temperature by immersing in an ice & salt mixture. (50% initial excess of glycerol removed) Glyceride mixture and cyclohexane dicarboxylic anhydride in 1.5:1 weight ratio was taken in the flask and heated to 80ºC for about 5 hours. The resin formed was stored in a refrigerator.

Scheme 2.1 Glycerolysis of linseed oil
2.1.2.2 Preparation of methyl acrylate co-polymers

The linseed oil resin was mixed with various concentration of methyl acrylate co-monomer and 2.5% (by weight) of benzoyl peroxide (initiator). 1 ml of TEGMA was added as cross linking agent and 2 drops of N, N-dimethyl aniline as accelerator. The mixture was then casted on a clean silicone oil spreaded glass mold and the mixture filled mold was placed in an oven at 50°C for 2 hours and the temperature was increased upto 100°C and curing takes place at this temperature for 2 hours and the sample was post cured for another one hour.

Scheme 2.2 Synthesis of Alkyd resin from linseed oil
Scheme 2.3 Synthesis of methyl acrylate (MA) co-polymers from linseed oil

Same procedure was followed for the preparation of various polymers by mixing the resin with different concentration of Methyl methacrylate (MMA), Vinyl acetate (VA) and N-vinyl -2-pyrrolidone (VP) co-monomers.
Scheme 2.4 Synthesis of methyl methacrylate (MMA) co-polymers from linseed oil
Scheme 2.5 Synthesis of vinyl acetate (VP) co-polymers from linseed oil
2.1.3 Synthesis of polymers from Sesame oil

Same procedure was followed for the preparation of various polymers from sesame oil using different concentration of methyl acrylate (MA), Methyl methacrylate (MMA), Vinyl acetate (VA) and N-vinyl -2-pyrrolidone(VP) co-monomers.
Scheme 2.7 Glycerolysis of Sesame oil

Mixture of mono and diglycerides
Scheme 2.8 Synthesis of Alkyd resin from Sesame oil

2.1.4 Synthesis of Inter Penetrating polymer network from linseed oil and sesame oil

Equal amount of alkyd resin of linseed oil and sesame oil was mixed with methyl acrylate (MA) co-monomer and 2.5% (by weight) of benzoyl peroxide (initiator). 1 ml of TEGMA was added as cross linking agent and 2 drops of N, N-dimethyl aniline as accelerator. The mixture was then casted on a clean silicone oil spreaded glass mold and the mixture filled mold was placed in an oven at 50°C for 2 hours and the temperature was increased upto 100°C and curing takes place at this temperature for 2 hours and the sample was post cured for another one hour.
Same procedure was followed for the preparation of various polymers by mixing the resin with other monomers like Methyl methacrylate (MMA), Vinyl acetate (VA) and N-vinyl-2-pyrrolidone (VP).

2.1.5 Synthesis of polymer composites from linseed oil

Alkyd resin of linseed oil was polymerized with 60% methyl methacrylate (MMA) co-monomer, 2% of the filler (sisal fiber) and 2.5% (by weight) of benzoyl peroxide (initiator). 1 ml of TEGMA was added as cross linking agent and 2 drops of N, N-dimethyl aniline as accelerator. The mixture was then casted on a clean silicone oil spreaded glass mold and the mixture filled mold was placed in an oven at 50°C for 2 hours and the temperature was increased upto 100°C and curing takes place at this temperature for 2 hours and the sample was post cured for another one hour.

Same procedure was followed for the preparation of various polymer composites by using other fillers like coconut fibre, wood flour and wheat flour.

2.1.6 Synthesis of polymer composites from sesame oil

Polymer composites from sesame oil was prepared by repeating the same procedure with 60% methyl acrylate co-monomer using the fillers like sisal fibre, coconut fibre, wood flour and wheat flour.

2.2 Physiochemical studies

2.2.1 Determination of Iodine value

The iodine value of animal and vegetable fats and oils measures the amount of -C=C- (double bonds) present in the product. The iodine value is expressed as gram of iodine (I\textsubscript{2}) absorbed per 100 gm of sample. Instead of I\textsubscript{2}, Iodine chloride (ICl) in acetic acid solution,
also known as Wij’s solution was used for this determination. The sample is made to react with an excess of Wij’s solution followed by determination of excess of Wij’s solution using a redox titration with sodium thiosulphate.

\[
\text{R-CH=CH-R + IBr}_{\text{excess}} \rightarrow \text{R-CHI-CHBr-R + IBr}_{\text{remaining}}
\]

\[
\text{IBr}_{\text{remaining}} + 2\text{KI} \rightarrow \text{KBr} + \text{KI} + \text{I}_2
\]

\[
\text{I}_2 + \text{starch} + 2\text{Na}_2\text{S}_2\text{O}_3 \text{ (blue)} \rightarrow 2\text{NaI} + \text{starch} + \text{Na}_2\text{S}_4\text{O}_6 \text{ (colorless)}
\]

The iodine value gives a measure of the average degree of unsaturation of a lipid: the higher the iodine value, the greater the number of C=C double bonds. Iodine value is directly proportional to the degree of unsaturation (No. of double bonds) and inversely proportional to the melting point of lipid. An increase in the iodine value indicates high susceptibility of lipid to oxidative rancidity due to high degree of unsaturation.

**Reagents required**

* Chloroform

* Wij’s solution (ICl / IBr)

* 15% potassium iodide solution

* 0.1 N Sodium thio sulphate solution

* Starch indicator (0.5 % aqueous solution)

**Procedure**

About 0.2 gram of the sample was weighed accurately in a chemical balance and transferred into a 500 ml iodine flask. 20 ml chloroform was added to the flask and swirl to dissolve the sample. 25 ml of wij’s solution was pipetted out into the flask. Stopper the flask and store it in a dark place for 30 minutes at room temperature. 100 ml of deionised water
and 20 ml of 15% KI solution was added and immediately titrate with 0.1 N sodium thio sulphate until the yellow colour almost disappeared. 1-2 ml of starch was added as indicator and the titration was continued until the blue colour just disappeared. Let this titer value (ie volume of thio for unreacted IBr) be A.

A blank titration was carried out without the sample, using the same quantity of the reagents. Let this titer value (ie volume of thio for blank) be B.

**Calculation**

The iodine value is calculated from the following equation:

\[
\text{Iodine value} = \left( B-A \right) \times N \times 12.7 / W
\]

Where,

- A is the volume of thio required for unreacted IBr in ml.
- B is the volume of thio required for the titration of the blank.
- N is the normality of thio solution.
- W is the weight of sample in gram.

### 2.2.2 Determination of Saponification value

The saponification value is defined as the number of milligrams of potassium hydroxide required for the saponification of one gram of the sample under specified conditions.

\[
\begin{align*}
\text{H}_2\text{C} & \text{O} - \text{C} - \text{R} \\
\text{HC} & \text{O} - \text{C} - \text{R} \\
\text{H}_2\text{C} & \text{O} - \text{C} - \text{R} \\
\text{H}_2\text{C} & \text{O} - \text{C} - \text{R} \\
\end{align*}
\]

\[+ 3 \text{ KOH} \rightarrow \begin{align*}
\text{H}_2\text{C} & \text{OH} \\
\text{HC} & \text{OH} \\
\text{H}_2\text{C} & \text{OH} \\
\end{align*} + 3 \text{ R} - \text{C} - \text{OK}
\]

**Scheme 2.9 Saponification reaction**
The saponification value is a measure of the sum of the free and hydrolysable acids in the fat or oil or alkyd. In the saponification reaction one mole of oil or fat reacts with three moles of KOH and leads to the formation of glycerol and sodium or potassium salt of fatty acid.

The saponification value of given sample is used for the determination of size, average molecular weight of the fatty acid and to estimate the non fatty acid impurities if present. It also gives an idea about the amount of alkali which would be accurately required by an oil or fat sample for its conversion into soap. Saponification value is inversely proportional to the molecular weight. Higher the saponification value of a fat, greater is the percentage of low molecular weight or short chain fatty acids. For simple alkyds of known type it provides a measure of the oil length.

**Reagents required**

*Standard hydrochloric acid solution (0.5N).*

*Potassium hydroxide solution (0.5N) in ethanol (95 per cent). This solution must be colourless or not darker than straw yellow.

*One per cent of phenolphthalein in ethanol (95 per cent). Other indicators with a colour change in the same pH range may be used also.

**Procedure**

About 1 to 2 gram of the oil was weighed accurately in a chemical balance and transferred into the 250 ml RB flask. Then alcoholic potash was added from the burette slowly to the flask. (30 ml each) It was then fitted with air condenser and heated in a water bath for about one hour. The flask was cooled and titrated against standard HCl solution
using phenolphthalein indicator. At the end point the solution was colourless. Let the volume of HCl required for excess alcoholic KOH be $V_1$.

A blank titration was done simultaneously with same quantity of alcoholic potassium hydroxide solution but without oil. The flask was cooled and titrated against standard HCl solution using phenolphthalein indicator. Let the volume of HCl for blank titration be $V_2$. Using these values the saponification values of oils and fats were determined.

**Calculation**

The saponification value is calculated from the following equation:

$$\text{Saponification value} = 56.1 \times \frac{(V_2 - V_1) N}{W}$$

Where,

- $V_1$ is the volume of hydrochloric acid required for the titration of the sample in ml.
- $V_2$ is the volume of hydrochloric acid required for the titration of the blank.
- $N$ is the normality of the hydrochloric acid solution.
- $W$ is the weight of sample in gram. [158]

**2.2.3 Determination of Acid value**

The acid value is defined as the number of milligrams of potassium hydroxide required to neutralize the free acids in one gram of the tested material (fat or oil) under test conditions.

$$\text{RCOOH} + \text{KOH} \rightarrow \text{RCOOK} + \text{H}_2\text{O}$$

The acid value is a measure of the free fatty acid groups in the fat or oil. Free anhydride groups are also partially measured. The content of anhydride groups in a finished alkyd is likely to be small but in samples of alkyd of high acid value taken in the early stage
of reaction it may be appreciable. In this case, the anhydride groups may be determined separately, or the acid and total anhydride groups determined by an alternative procedure in which the latter are fully hydrolyzed. The acid number of the varnishes or resin solutions should be expressed on the basis of solid components, not on the solution. Usually, the acidity is due to the presence of carboxylic groups from free fatty acids or acids used in polyester production.

**Reagents required**

- Standard potassium hydroxide solution (0.1N) in methanol.
- One per cent of phenolphthalein in ethanol (95 per cent). Other indicators with a colour change in the same pH range (8.3—10) may be used also.
- Neutralized ethyl alcohol.

**Procedure**

About 0.2 to 0.5g of the sample was weighed in 250 ml conical flask. 50 ml of neutralized ethyl alcohol was added to the sample. The mixture was heated on a water bath to dissolve the sample. The solution was titrated against 0.1N potassium hydroxide solution using phenolphthalein as indicator. Appearance of pink colour is the end point.

**Calculation**

The acid value is calculated from the following equation:

\[ \text{Acid value} = \frac{56.1 \times A \times N}{W} \]

Where,

- \( A \) is the volume of potassium hydroxide solution consumed in ml.
- \( N \) is the normality of the potassium hydroxide solution.
- \( W \) is the weight of sample in gram.
2.2.4 Determination of Hydroxyl value

The hydroxyl value is defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid taken up on acetylation of one gram of the sample. The hydroxyl content is commonly expressed in these units, in conformity with the acid and saponification values.

For comparison with hydroxyl contents determined by methods other than acetylation, e.g. active hydrogen or infrared spectroscopic methods, the hydroxyl content may be expressed as the percentage of hydroxyl groups, by multiplying the hydroxyl value by the factor 17/560.

Determination of the free hydroxyl groups present in the alkyd, these being present as free polyhydric alcohol, partial esters, polyester end groups or hydroxylated fatty acids.

Reagents required

*Standard potassium hydroxide solution (0.5N) in methanol or ethanol.
*Acetyling reagent: Acetic anhydride AR and pyridine are mixed in 1:3 ratio (by volume). The mixture is transferred to a burette provided with soda lime guard tube.
*One per cent of phenolphthalein in ethanol (95 per cent).

Procedure

Two 250 ml conical flasks marked as A and B were taken and fitted with reflux condenser through either ground glass joints or rubber stopper. Introduce accurately weighed sample (about 1gm) in flask A and then 10 ml of the mixture of acetic anhydride and pyridine was added to the flask A and also to the blank flask B. Reflux the two flasks on boiling water bath for about 30 minutes. The flask was allowed to cool and then 20 ml of distilled water
was added to each of the flask. Down the condenser, while shaking the flasks to ensure thorough mixing and continue the heating for 2-5 minutes.

The flask was cooled and allowed to stand for about 10 minutes. The content of each flask was titrated separately with standard 0.5N alcoholic KOH solution using phenolphthalein indicator. A thorough shaking of the flask is necessary during the titration to ensure complete neutralization of the acid. The difference between the volumes of KOH used in the two titrations corresponds to the alcohol.

**Calculation**

The hydroxyl value is calculated from the following equation:

\[
\text{Percentage of Hydroxyl group} = \frac{(V_1 - V_2) \times 17.01 \times 100}{W \times 1000}
\]

Where,

- \( V_1 \) is the volume of potassium hydroxide solution required for the titration of the blank.
- \( V_2 \) is the volume of potassium hydroxide solution required for the titration of the sample.
- \( N \) is the normality of the alcoholic potassium hydroxide solution.
- \( W \) is the weight of sample in gm.

**2.2.5 Determination of Intrinsic viscosity**

Viscosity is an internal property of a fluid that offers resistance to flow. It is due to the internal friction of molecules and mainly depends on the nature and temperature of the liquid. The Ostwald method is a simple method for the measurement of viscosity, in which viscosity of liquid is measured by comparing the viscosity of an unknown liquid with that of liquid
whose viscosity is known. In this method viscosity of liquid is measured by comparing the flow times of two liquids of equal volumes using same viscometer.

Consider two liquids are passing through a capillary of same viscometer. Then the coefficient of viscosity of liquid (\( \eta_2 \)) is given by equation

\[
\eta_2 = \frac{\eta_2 \rho_2 t_2}{\rho_1 t_1}
\]

Here \( t_1 \) and \( t_2 \) are the time of flow of the liquids and \( \rho_1 \) and \( \rho_2 \) are the respective densities. And \( \eta_1 \) is the coefficient of viscosity of water.

**Procedure**

Intrinsic viscosity of the oil, monoglyceride and the alkyd resin of both linseed oil and sesame oil were determined by using Ostwald viscometer. In this technique, the time was measured for the dilute solution of oil, monoglyceride and the resin to flow through a capillary tube. Through measuring the flow times at various concentrations and comparing with the flow time obtained for the pure solvent, it is possible to obtain the value for intrinsic viscosity (or limiting viscosity number) \([\eta]\). The specific viscosity (\(\eta_{sp}\)) at different concentrations was measured and the intrinsic viscosity \(\eta_{intrinsic}\) was obtained by extrapolating the linear plot of \(\eta_{sp}/C\) verses concentration \(C\) to the zero concentration.

**Calculation**

The specific viscosity and intrinsic viscosity of the oil, glycerides and alkyd resin were calculated from the following relations:

\[
\frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_{intrinsic} - 1 = \eta_{sp}
\]

Specific Viscosity =
Reduced Viscosity = \frac{\eta_{sp}}{C} - \eta_{ref}

2.2.6 Determination of specific gravity

Specific gravity is the ratio of the weight of a given volume of a substance to the weight of an equal volume of some reference substance. The reference substance is always water at its densest, (4°C) for liquids.

Procedure

First the specific gravity bottle was washed and dried in an oven. Cool for a while and weight of this bottle was taken using an electronic balance. Note this weight. Then the bottle was filled with distilled water and inserts the stopper without entrapment of air bubble. Remove any water which has extruded from capillary opening and weight of the specific gravity bottle was taken with distilled water. Then water is removed from the bottle, dried in air oven and cool for a while. Note this weight. Again fill the specific gravity bottle with linseed oil and the weight was taken.
Calculation

The specific gravity of oil was calculated using the following equation:

Specific gravity = weight of linseed oil/weight of distilled water.

The same procedure was followed to determine the specific gravities of sesame oil, glycerides and alkyd resin of both linseed oil and sesame oil.

2.3 Characterization of polymers

2.3.1 Swelling analysis

The swelling analysis of the polymeric samples were carried out in different solvents viz., saline (20% NaCl), alkaline (2% NaOH), acidic (2%H₂SO₄) and toluene. The polymeric samples were allowed to remain in the solution for 72 hours at room temperature and then weighed as soon as they were removed from the solvent. The samples were weighed after 2, 4, 6, 8, 12, 24, 48 and 72 hours. The swelling ratio, qᵥ of various polymers at equilibrium [159] was determined using the Equation

\[ qᵥ = \frac{\text{volume of swollen polymer}}{\text{volume of dry polymer}} \]

2.3.2 Chemical resistance

Chemical resistance of the newly prepared polymer samples were studied by immersing the polymer samples in various solvents such as CCl₄, CHCl₃, diethyl ether, benzene, toluene, H₂O₂, HCl, ethanol, H₂O, NaCl etc. and measuring the dimensional changes after 1 week and 4 weeks[160]. The weight loss also measured after 30 days.
2.3.3 Biodegradation - Soil Burial test

Biodegradation of the polymer samples prepared from linseed oil and sesame oil were studied by soil burial test. For the soil burial test the replicate pieces of the sample (5 x 3 cm) were buried in the garden soil at the depth of 30 cm from the ground surface for 3 months, inoculated with the sewage sludge having ability to adhere and degrade the polymer film (Gandini, 2008). The test specimen was periodically removed from the soil and the specimen was then gently washed to remove attached soil and dust after being dried in vacuum oven. The extent of degradation was examined by measuring the weight loss after 30 and 60 days which is calculated using the relation, [161]

\[
\text{Degree of biodegradation, } D = \frac{(M_o - M_t)}{M_o} \times 100
\]

Where,

- \( M_o \) – weight of original film
- \( M_t \) – weight of residual film after degradation for different time.

2.3.4 Photo degradation of polymers

Photo degradation of the polymer samples prepared from both the linseed oil and sesame oil were studied by exposing the polymer samples to direct sun light (dry and wet condition) and UV light and measuring the changes in the mechanical properties. The extent of degradation was examined by measuring the weight loss after 30 and 60 days. The changes in tensile strength of the polymer samples after irradiation were measured at one week time interval.