

THERMAL AND MECHANICAL STUDIES OF POLYMER SUPPORTED POLYESTERS FROM MUSTARD OIL MONOMERS METHYLMETHACRYLATE AND VINYL ACETATE

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Abstract : *Polyesters were synthesised from naturally available mustard oil. Plant oil such as mustard oil has been used for the preparation of polyesters for its several applications. Epoxidation of Mustard oil (EMO) has been carried out by per acetic acid method. Further mustard acrylated epoxy resin (MUAEP) were synthesised from (EMO) and it is characterised by physicochemical properties. The polyesters are prepared by using co-monomers like MMA ratio and Vinyl acetate ratio. These polymers were characterised by Spectral analysis, FT-IR, H¹NMR, Thermal studies, TG-DTA, Mechanical properties, Biodegradation and Chemical resistance. The outcome of the studies revealed that the newly prepared polyesters are potential biodegradable material for various consumer applications like package materials, sporting goods and floor mats.*

Key words : Mustard oil, Epoxidation, Thermal analysis, Tensile strength, Mechanical properties, Biodegradation, Chemical resistance.

Introduction

Polymers are multi-disciplinary science that deals about the synthesis and their chemical properties. The polymers obtained from edible oils (mustard oil) are bio-polymers which are generated from the renewable natural source and they are often referred to as bio-degradable polymers. Bio-polymers obtained from edible oils are flexible and rubbery. These polymers are non-toxic in nature. (1)

Essential oils are oil based polymers having many advantages compared with the polymers prepared from petroleum-based monomers. They are bio-degradable and in many cases cheaper than petroleum polymers. Vegetable oil constituents are complex multi-component mixtures of different triglycerols (2). Different essential oils and oil based formulations are reported to be efficient antimicrobial agents that can be used to prevent food spoilage. The antibacterial activity may be due to the ability of oil components to damage the bacterial membranes and hence resulting in lysis of the cell. Mustard oil is a food grade oil that is reported to have antibacterial property (3).

Polymers have made a considerable impact in various fields of biomedical engineering including tissue engineering and drug delivery where cell-seeded constructs are designed to replace damaged (or) diseased tissues (3,4). Vegetable oils are triglycerides of fatty acids and they are excellent source of raw materials for the preparation of original polymeric materials with the objectives to replace petro-chemical based polymers and also to develop materials for certain applications (5,6).

In recent year, there has been a large amount of demand for plant oils as an alternative resource for the production of additive for various applications such as polymer, coating, adhesive and nanocomposite (7,8). The development of polymers has a significant effect on everyday life. Polymers are used as replacements for woods, glass and metals.

Mustard oil contains the least amount of saturated fatty acids. The aim of the present study is the physicochemical properties of mustard oil. Mustard oil polymers are also analysed by FT-IR and NMR.

2. Experimental

2.1 Materials and methods

Mustard oil was purchased from local super market. Hydrogen peroxide (H_2O_2), glacial acetic acid, Triethylene glycol dimethylacrylate (TEGMA), methylacrylate, Vinyl Acetate, benzene, N,N – dimethyl aniline, benzoyl peroxide were purchased from Sigma Aldrich Co and used as such.

2.2 Formation of Acrylated epoxidised Mustard oil

Mustard oil was epoxidised by using glacial acetic acid and hydrogen peroxide (H_2O_2) and they were taken in a three necked round bottomed flask. Hydrogen peroxide was added in drops through a dropping funnel for 2 hours. The reaction mixture was refluxed with constant stirring for 10-12 hours at 70^0-80^0c . The epoxidised resin was separated and washed with warm water to remove the glacial acetic acid present. The epoxidised mustard oil was then acrylated by using acrylic acid, triethyl amine was used as catalyst. Here benzene acts as solvent. The reaction mixture was again refluxed at 70^0-80^0c and finally the acrylated epoxy mustard oil resin was obtained.

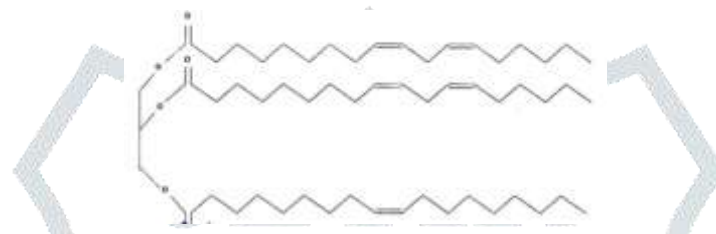


Figure 1 a : Structure of Mustard Oil

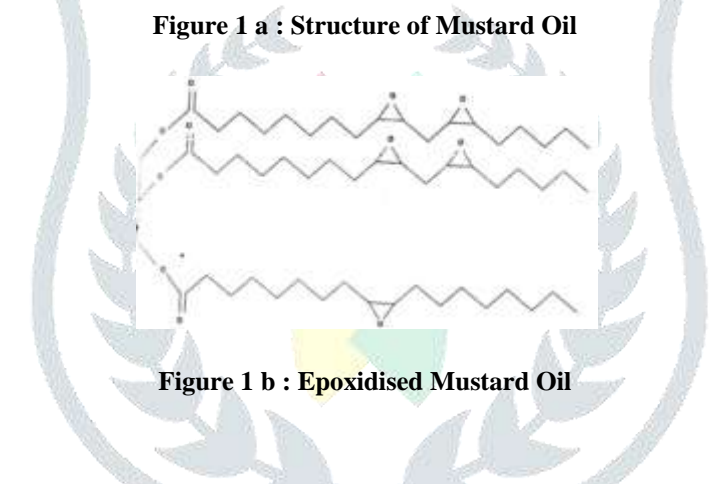


Figure 1 b : Epoxidised Mustard Oil

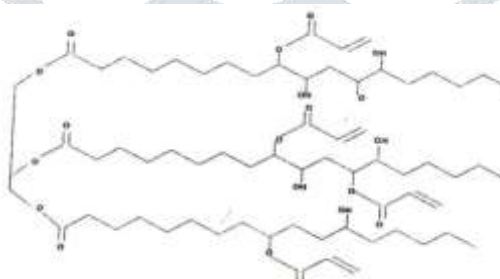


Figure 1 c : Acrylated Mustard Oil

2.3 Polymer synthesis

The resin thus prepared was polymerised with different concentrations of monomers such as methylmethacrylate and Vinyl Acetate at the ratio of 1:3 using benzoyl peroxide as catalyst. Triethylene glycol dimethyl acrylate (TEGMA) was added as a cross linking agent. The mixture was then casted on clean silicon oil spreaded over a glass plate. Then, it is placed in air oven and maintained at a temperature 100^0c for about 3 hours.

The procedure was followed for the preparation of various polymers by mixing the resin with different concentration of methylmethacrylate co-monomer. All the cured materials showed high toughness, elastomeric and good transparency.

3. Characterization

3.1 Spectral Studies

The formation of epoxy resin from oil was studied by FT-IR and ^1H NMR spectroscopy. FTIR spectral studies were performed by using Perkin Elmer spectrometer and ^1H NMR spectra were recorded on Broker Avance spectrometer.

3.2 Mechanical Studies

The tensile strength of the biopolymers prepared was determined by using Instron UTM (dumbbell shaped cut). It is a 10 ton Universal Testing Machine. The values represented were mean of about 3-4 samples. The new polymeric materials exhibit tensile stress-strain behaviour relatively to plastics. The cross linked densities were determined from the rubbery modulus plateau based on the theory of rubber elasticity

$$E^1 = 3\gamma eRT \quad (9,10)$$

Where,

“ E^1 ” is the storage modulus (Young's) of cross linked polymer in the plateau region.

“ R ” is the universal gas constant ($8.314\text{J mole}^{-1}\text{K}^{-1}$).

“ T ” is the absolute temperature (K)

“ γ ” is the cross linked density.

3.3 Thermal Studies

The TG/DTA thermograms of the post polymers were obtained at a scanning speed of $10^\circ\text{C min}^{-1}$ in the temperature range of 30°C - 700°C under the flow of a nitrogen gas atmosphere by using Perkin Elmer Diamon thermo gravimetric analyser.

3.4 Bio-degradation soil burial test

Bio-degradation of polymers was studied by soil burial test. For the soil burial test replicate pieces of the sample ($5 \times 3\text{cm}$) were buried in the garden soil at the depth of 30cm from the ground surface for 3 months. It is inoculated with the sewage sludge having the ability to adhere and to degrade the polymer film. The test specimen was periodically removed from the soil and the specimen was gently washed to remove the attached soil and dust after it is being dried in vacuum oven. The extent of degradation was examined by measuring the weight loss after 30 and 60 day's which is calculated by using the relation (11)

Degree of biodegradation,

$$D = \frac{W_o - W_t}{W_o} \times 100$$

Where;

W_o – Weight of the original film,

W_t – Weight of residual film after degradation for different time.

3.5 Chemical resistance

Chemical resistance of the newly prepared polymer sample were studied by immersing the polymer sample in various solvents such as CCl_4 , CHCl_3 , CH_3COCH_3 , DMSO and Chlorobenzene etc. and the dimensional changes are measured after 15 days and 45 days (12) and at last the weight loss is also measured after 45days.

4. Results and Discussion

4.1 Spectral analysis

4.1.1 IR Spectral studies

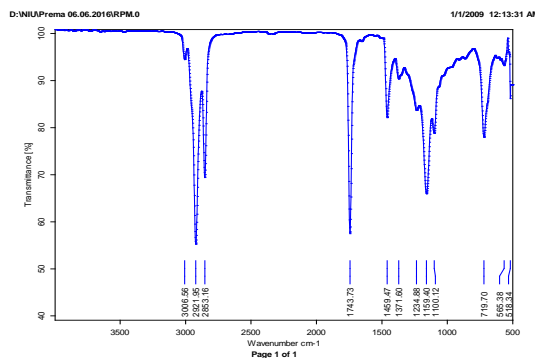


Figure 2 a : FTIR Spectra of Mustard Oil

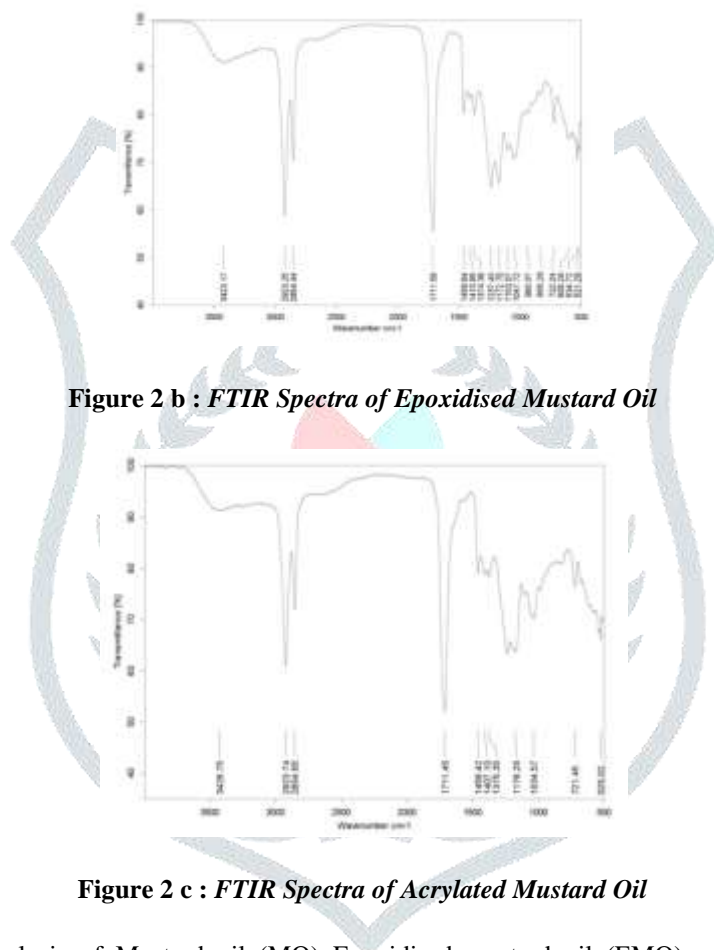


Figure 2 b : FTIR Spectra of Epoxidised Mustard Oil

Figure 2 c : FTIR Spectra of Acrylated Mustard Oil

The FT-IR Spectral analysis of Mustard oil (MO) Epoxidised mustard oil (EMO) and Acrylated mustard oil resin (AMOR) as shown in figure (2a,2b,2c) shows peak at 3006.56cm^{-1} , 2921.95cm^{-1} , 2853.16cm^{-1} corresponds to the C-H stretching frequencies for olefinic, methylene and methyl groups (13). The peak at 1743.73cm^{-1} corresponds to the C=O stretching frequencies for ester group. The peak at 1459.47cm^{-1} , 1371.60cm^{-1} and 719.70cm^{-1} corresponds to the C-H bending vibration of CH_2 & CH_3 groups.

The Epoxy group shows three characteristic absorption peaks at $1240\text{-}1250\text{ cm}^{-1}$, $950\text{-}860\text{ cm}^{-1}$ and $865\text{-}785\text{cm}^{-1}$. The region of the first peaks is small and lies at $1240\text{-}1250\text{ cm}^{-1}$. The peak at 1237cm^{-1} and $960.07\text{-}865.26\text{cm}^{-1}$ (Fig 2b) which corresponds to the epoxy group. The particular peak disappeared in the acrylated epoxy resin. The peak obtained at $865.26\text{-}722.34\text{cm}^{-1}$ in the epoxy resin correspond to the stretching vibration – $\text{CH} =$ and CH_2 Groups.

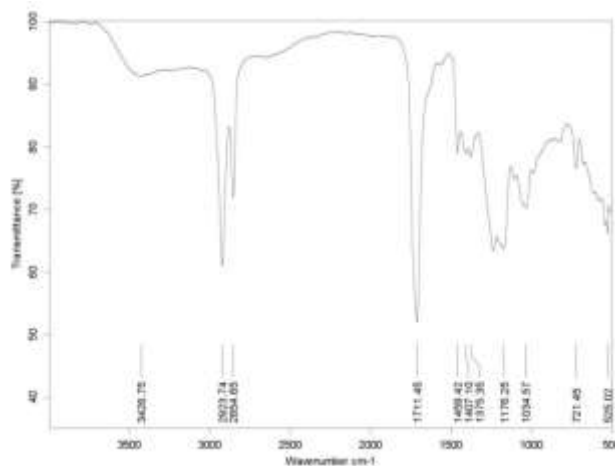


Figure 2 c : FTIR Spectra of Acrylated Mustard Oil

4.1.2 ¹H-NMR spectral studies Mustard oil Epoxidised Mustard oil Acrylated Mustard oil

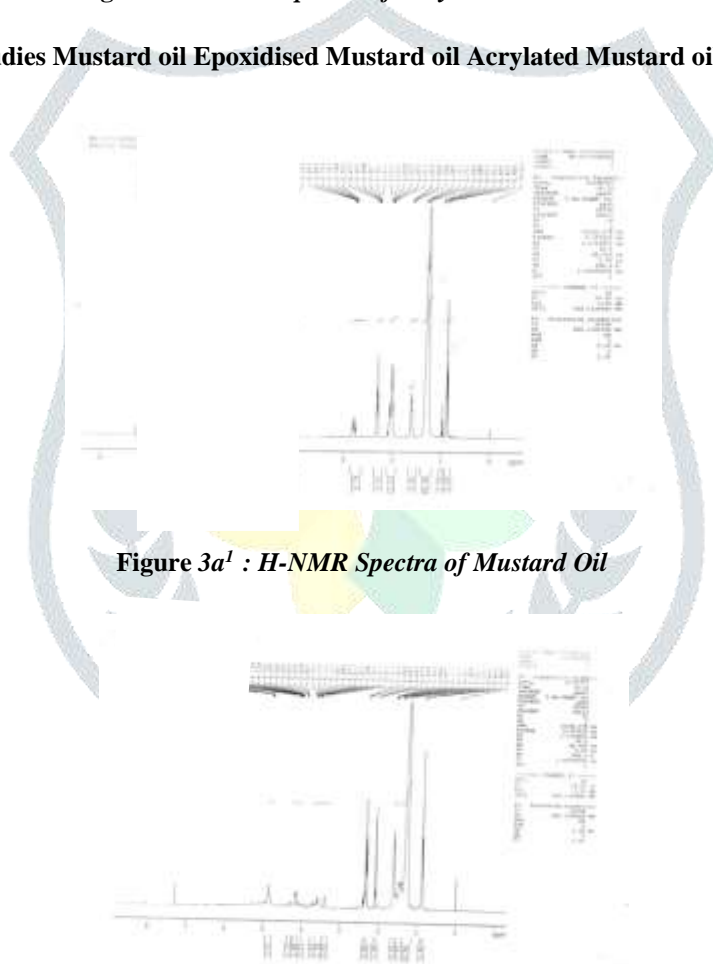


Figure 3a¹ : H-NMR Spectra of Mustard Oil

Figure 3b¹: H-NMR Spectra of Epoxidised Mustard Oil

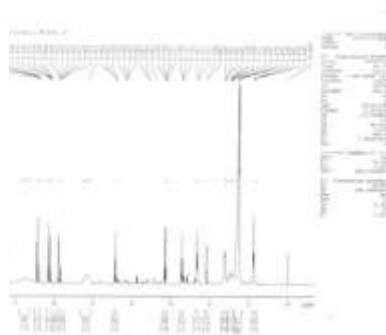
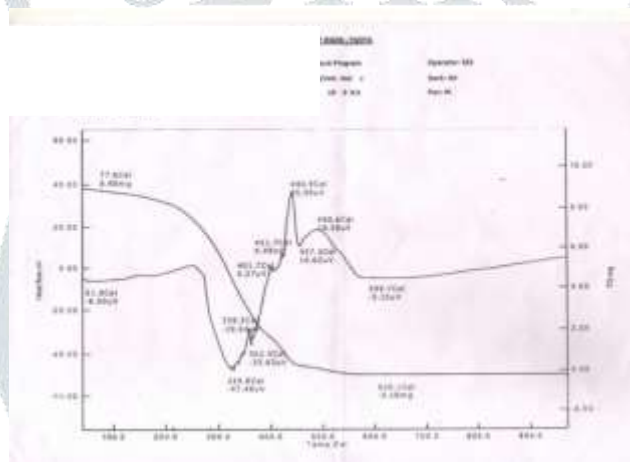


Figure 3c¹: $^1\text{H-NMR}$ Spectra of Acrylated Mustard Oil

In the $^1\text{H-NMR}$ spectrum the peak at 4.1-4.3 ppm originates from the protons in the methylene group. The peaks 5.2-5.3 ppm indicates the unsaturated vinylic hydrogens. The peak 5.4 ppm indicates the presence of unsaturation in the oil. These peaks will disappear in the epoxy resin and reappears in acrylated epoxy sample. The proton in the CH_2 group between two carbon-carbon double bonds appears at 2.7-2.8 ppm (14). This peak disappears in epoxy resin and shifted to 3.1-3.4 ppm in the acrylated epoxy resin due to hydroxyl and carboxylate ester linkages (15). The strong peak at 1.3 ppm is attributed to the long chain. The peak at 0.95-2.3 ppm is due to the long aliphatic side chain (16).

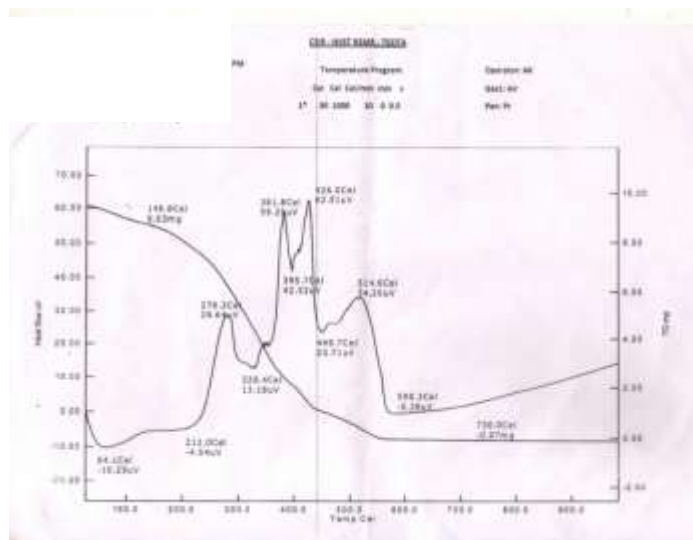
4.2 Thermal Analysis



Thermo gravimetric analysis (TGA) is used to investigate the thermal stability of the polymers. The Fig (4a,4b) shows the decomposition behaviour of the polymer sample MUMMA (1: 3) and MUVA under nitrogen atmosphere. Two distinct temperature regions are observed by the samples experienced with significant weight loss (200-280°C and 390-450°C).

It is clear from the figure that most of the unreacted free oil disappears at the temperature between 200°C and 280°C (stage 1) and this region corresponds to the evaporation of the unreacted free oil. On the other hand, the insoluble substances were found to be highly cross-linked thermosets that decompose at temperatures greater than that of 390-450°C (stage 2). This decomposition stage corresponds to the carbonization of the cross linked polymer network.

Stage 1 in the TGA curves involves two major steps (i.e.) diffusion of the free oil to the surface of the bulk polymer and subsequent evaporation. The diffusion of the free oil is retarded by cross linked materials, but the evaporation of the free oils from the surface occurs rather rapidly at high temperatures. From the proceeding results it is clear that the thermal stability of the polymer is limited by the first decomposition stage in the TGA thermo grams, which is directly related to the amount of unreacted free oil in the bulk polymer.



Stage 1 in the DTA curve of mustard methylmethacrylate polymer the peak at 270^oc owing to the glass transition temperature and the endothermic peak at 329.8^oc correspond to the crystallisation of the polymer network. Two exotherms are seen in the sample. The 1st exothermic peak at 440^oc in sample is relatively weak and it corresponds to the cleavage of the long allyl side chain, the second exothermic peak at 490.6^oc in the sample is strong and it corresponds to the decomposition of char formation of cross linking polymer network.

Similarly in the DTA curve of vinyl acetate polymer, the peak at 212.0^oc owing to the glass transition temperature and the endothermic peak at 328.4^oc corresponds to the crystallisation of polymer. Two exothermic peaks are seen in the figure. The first exothermic peak 381.8^oC ranging from 390-370^oC. The second exothermic peak 426^oC ranging from 430-400^oC. Comparing the DTA curves the crystallisation of MMA (1:3) ratio was greater than vinyl acetate.

4.3 Mechanical properties

The Mechanical properties of the polymer samples prepared are shown in Table 1. From the data, it is known that the polymer samples prepared are having very high tensile strength and modulus relative to other thermosetting plastics. Comparing the two samples analysed, methylmethacrylate polymer is having high tensile strength and modulus. The mechanical properties of sample of vary from rubber to hard plastics.

TABLE 1 : Mechanical Properties of Polymer Samples

POLYMER SAMPLE	CROSS LINK DENSITY	TENSILE STRENGTH X10 ⁵ Pa	% OF ELONGATION	YOUNG'S MODULUS X10 ⁵ Pa
MUMMA (1:3)	1.30	3.714	3.24	417.39
MUVA (1:1)	4.10	1.071	2.6	162.16

4.4 Bio-degradation (soil burial test)

Bio degradation of the polymer sample prepared by the free radical co polymerization of mustard oil, epoxy resin and acrylated epoxy resin of mustard oil with various concentrations of monomers like methylmethacrylate, Vinyl acetate ratio is reported in the table 2.

TABLE 2 : Percentage of Bio-Degradation of polymer sample

POLYMER	DEGREE OF BIODEGRADATION
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SAMPLE	WEIGHT LOSS %	
	30 DAYS	60 DAYS
MMA (1:3)	18.5	35.26
MUVA	14	20

From the data obtained by soil burial test, it is known that, the extent of biodegradation increases with decrease in the concentration of monomer. From this data bio degradation is high for methylmethacrylate polymer

4.5 Chemical Resistance

Chemical Resistance of the polymer at various chemicals are determined by immersing the polymer sample in different media and measuring the dimensional change after 45days. The weight loss can be calculated.

Table 3 & 4 shows the weight loss of polymer samples after 45 days. The comparison of stability of polymers MMA and Vinyl Acetate towards various chemical was shown in table 3 & 4. From this table all the polymeric samples prepared are highly stable, but undergoes degradation in 1,2 dichlorobenzene of acetone. The dimension of the polymers immersed in organic solvents of DMSO, CCl₄ and CHCl₃ slightly changes due to their fragility.

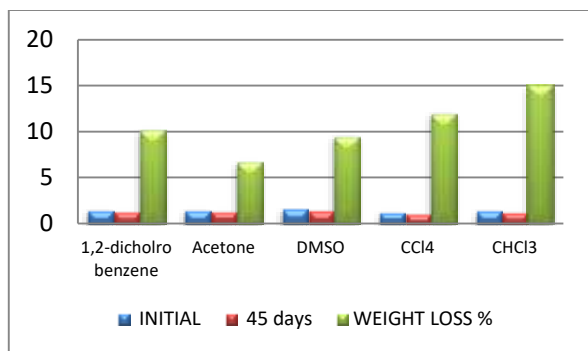
TABLE 3 : Chemical Resistance of MMA polymer

SL. NO	SOLVENT	INITIAL	45 DAYS	WEIGHT LOSS %
1.	1,2 dichloro Benzene	1.47	1.32	10.2
2.	Acetone	1.48	1.38	6.75
3.	DMSO	1.614	1.46	9.5
4.	CCl ₄	1.24	1.09	12
5.	CHCl ₃	1.45	1.26	15

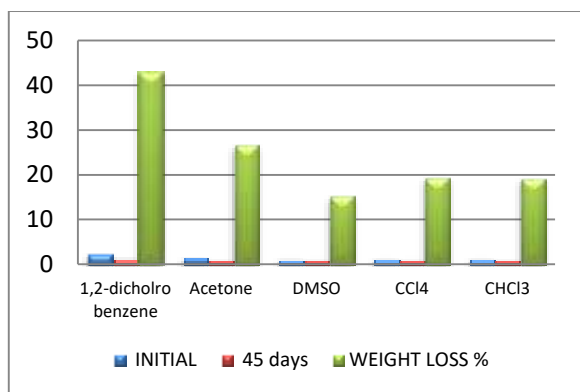
TABLE 4 : Chemical Resistance of Vinyl Acetate polymer

SL. NO	SOLVENT	INITIAL	45 DAYS	WEIGHT LOSS %
1.	1,2 dichloro Benzene	2.42	1.37	43
2.	Acetone	1.45	1.06	26.8
3.	DMSO	1.20	1.01	15.4
4.	CCl ₄	1.28	1.03	19.5
5.	CHCl ₃	1.30	1.05	19.2

GRAPH 1 : Chemical resistance of MMA (1:3) Polymers



GRAPH 2 : Chemical resistance of MUMA Polymers



Conclusion

Polymers are widely used in modern society, because they are light in weight, low in cost and easy to process materials. The purpose of this work is to prepare high molecular weight polymers and it is also an alternative to petroleum based polymeric materials that ranges from soft and flexible rubbers to ductile (or) rigid plastic, as well as it shows high performance. Natural oils are expected to be inexpensive renewable resources. Thus, renewable resources are greatly favoured for the production of polymers. The wide ranges of mechanical properties like Stress-Strain behaviour, tensile strength and toughness are used as wide consumer applications. All the polyesters have good thermal and mechanical properties. Mustard oils are triglycerides of fatty acids. It contains unsaturated groups and it is also used in the preparation of epoxides and polymers.

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