

Preparation of Biobased Copolymer from Acrylated Epoxidized Soyabean Oil with Other Known and Synthesised Monomers

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Abstract

The objective of this research is to develop biobased copolymer from epoxy soybean oil. Triglyceride based copolymers are produced from free radical copolymerization between acrylated epoxidized soybean oil (AESO) and Glycidyl methacrylate, styrene, methyl methacrylate and n butyl methacrylate. AESO has been produced by acrylation reaction with acrylic acid. Triethylamine has acted as catalyst and hydroquinone as a free radical inhibitor. The acrylate groups in soybean oil have been determined by using the nuclear magnetic resonance spectroscopy (1H-NMR). Copolymerisation of AESO with above mentioned monomers as a comonomer done to form rigid polymer using benzoyl peroxide as a free radical initiator. The mixture has been cured at 90-100°C for 30 min in the oven. The biopolymer prepared as copolymer, is characterized by using the Fourier transform infrared spectrometer (FTIR) to confirm molecular structure

Keyword: AESO- Acrylated epoxidized soybean oil, CE- Chain Extender, Copolymer

1. Introduction

Sustainable and biodegradable polymers become essential in the current era. Biodegradable polymers have a tendency to degrade biologically, and their rate of degradation with time depends on the available environment [1]. To improve the properties of blends and compounds of biopolymers, and to resolve the issue of miscibility with each other, the development of additives called “chain extenders” has been driven [2]. Chain extension is a method to obtain higher molecular weight polycondensates through a post-polymerization reaction carried out either in the final polymerization processing step or during compounding, extrusion, or injection molding of the final product [3]. Chain extension with designed multifunctional polymers is introduced to enhance the properties of sustainable (bio)polymers, such as PLA and PBAT, PBS, PBST, enabling them to become compatible with each other for new polymers in demanding applications. Moreover, these chain extenders are also able to compatibilize biopolymers with traditional engineering plastics. In present time, the demand for a sustainable circular plastic economy has increased due to dependency on petroleum-based conventional resources and their non-biodegradable applications. This has encouraged scientists to prepare and develop biodegradable polymers and additives for them to replace non-degradable polymers with easily available, renewable, and inexpensive natural resources, such as vegetable oils, which are becoming important. Nowadays, researchers have focused on soybean oil and its derivatives to synthesize new bio-based polymers, such as epoxidized soybean oil

(ESO), acrylated epoxidized soybean oil (AESO) [4,5]. In the current research, the ESO reacted with acrylic acid to form AESO. The resulting monomer was then copolymerized with other known and synthesized monomers to form a copolymer. The resultant copolymer can be useful as chain extender to improve properties of degraded polymers. We all know that Glycidyl groups can react with materials containing active hydrogens, such as an amino group, a hydroxyl group, and a carboxyl group. It shows promise that the polymer with the glycidyl groups forms linkages by reacting with other polymers containing amino or carboxyl groups. The copolymer synthesized from glycidyl methacrylate and styrene (PGS) contains glycidyl groups and phenyl groups. Long-chain hydrocarbon from BDO and triglyceride provides some flexibility to the copolymer. There is a chance of very little hydrolysis of the glycidyl group takes place during polymerization. It needs a high temperature (200°C) to make hydroxyl–glycidyl and carboxyl–glycidyl reaction. The copolymer of glycidyl methacrylate and styrene (PGS) was synthesized here along with acrylated epoxidized soybean oil, methyl methacrylate, and acrylated BDO. [6] Biobased copolymer synthesised here could be very much useful as chain extender or coupling /crosslinking agent during compounding or blending of biopolymers having -COOH and -OH terminal end group e.g. PBAT/PLA. Reactive additives allow for improving properties of thermoplastic polymers during processing and for their later use. The chemical modification using multifunctional epoxide styrene-acrylic chain extenders (CE) in reactive processes is by now an established method to prevent degradation and to improve the processability as well as the final properties of thermoplastics. The CE incorporation leads to increased shear viscosity, higher melt strength and induces strain hardening due to the formation of branched chains and/or even crosslinking. The crystallization is also directly influenced by the changed chain topology.[7] A quite convenient method to individually adjust the rheological properties of polymers for certain purposes is the reactive melt modification with appropriate chemical agents. The most popular of these so-called chain extenders (CE) is the multifunctional styrene–acrylic oligomeric chain extender. The chain extender is useful in injection molding and extrusion processes with virgin, post-industrial recycled and/or post-consumer recycled polyesters such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT), as well as polyamides (PA), bisphenol A-based polycarbonates (PC), thermoplastic polyurethanes (TPU), polyoxymethylene (POM) and blends made out of it to counteract degradation effects. Yet, it is also widely used with other polyester polymers such as polylactide (PLA) and Poly butylene adipate co terephthalate which nowadays widely used for replacing single-use plastic commodities due to its degradable nature in industrial composting conditions. Figure -1 & 2 given below shows use of chain extender.

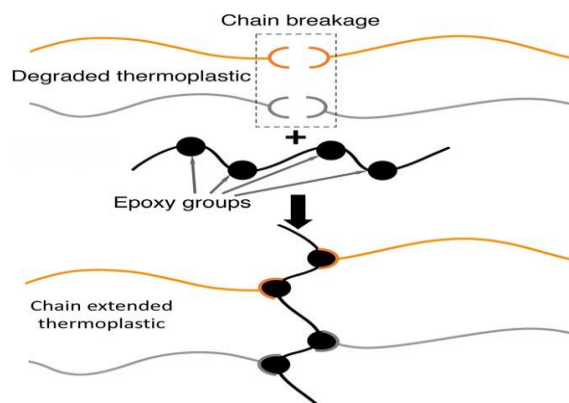


Fig – 1 Application of CE in polymer chain

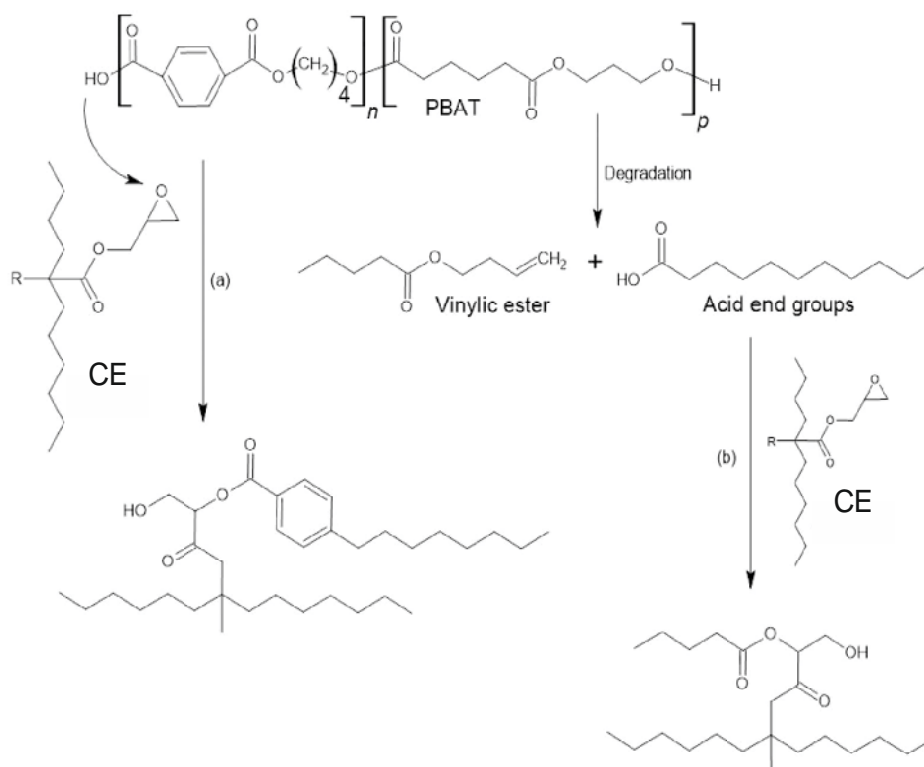


Fig -2 Use of CE with PBAT

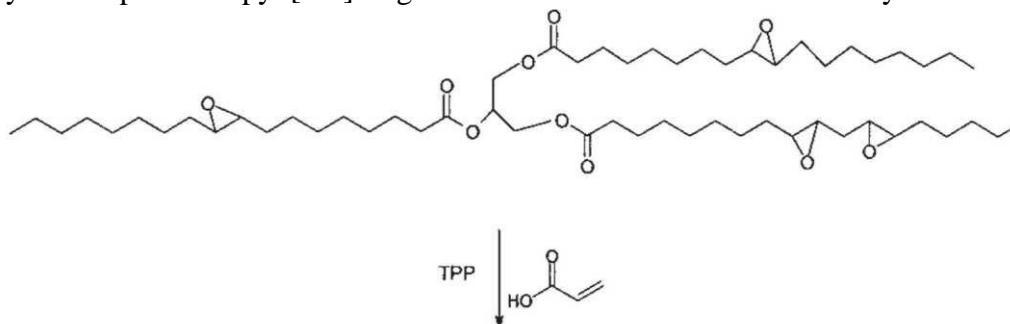
2. Material

Epoxidized Soyabean oil purchased from Rainbow Drugs & Chemicals with epoxy equivalent value 6.5, Acrylic acid, Triethylamine, Methacrylic acid, Glycidyl methacrylate, Styrene, Hydroquinone, Benzoyl peroxide purchased from Jayesh K chemical Ahmedabad. 1,4 Butane diol and Tetra -n- butyl titanate purchased from Sunny Enterprises. Toluene purchased from local supplier.

2.1. Experimentals

2.1.1. Acrylated epoxidized soybean oil synthesis:

AESO were synthesized from the reaction of acrylic acid with epoxidized soybean oil supplied by Rainbow Drugs & Chemicals., which has an epoxy functionality of 6 epoxy rings per triglyceride. Hydroquinone was added as a free radical inhibitor in the amount of 0.04 wt% of the total weight of the reactants. In addition, triethylamine was added to act as a catalyst in the amount of 0.5 wt% of the total weight of the reactants. This mixture was reacted at 95°C for 12 h. The number of acrylates/triglycerides of resulting AESO can be determined by 1H-NMR analysis. The acrylated functional group was determined by FTIR spectroscopy. [8-9]. Fig -3 shows reaction mechanism of acrylation of ESBO.



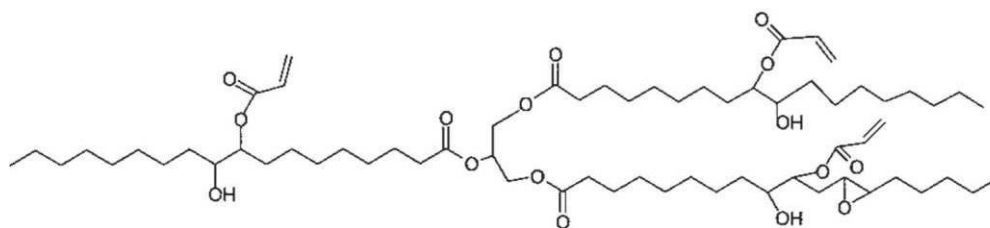


Fig – 3 Acrylation of ESBO

2.1.2. Hydroxy Butyl methacrylate Synthesis:

Experiment was carried out in 500 ml round bottom flask in which 1 mole of Methacrylic acid was taken with 0.5% Hydroquinone as free radical inhibitor. 1 mole of 1,4 Butanediol was pumped slowly into the flask. The mixture was reacted for 24 to 36 hours. Tetra-n-butyl titanate was used as catalyst for esterification. Resulting product was sent for FTIR, has confirmed esterification product.[10]. Fig-4 shows reaction mechanism of acrylation of 1,4 BDO.

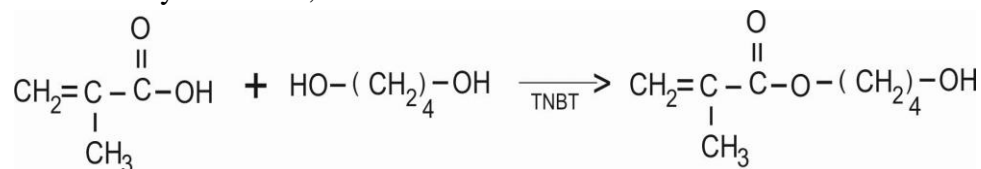


Fig -4 Reaction-1,4 BDO with methacrylic acid

2.1.3. Copolymerisation:

The product obtained as AESO has been used as a comonomer along with Styrene, Methyl methacrylate, Glycidyl methacrylate and product obtained from esterification of 1,4 butanediol and methacrylic acid. Polymerisation carried out in a three necked round bottom flask. Benzoyl peroxide used as a free radical initiator and Hydroquinone used as a inhibitor to achieve desire molecular weight of the resultant copolymer. Toluene used as a solvent. Reaction carried out at 98⁰ C for 300 minutes. Vacuum was applied to remove solvent and temp raised to 140⁰ C to ensure maximum removal of solvent. The product obtained was sent for NMR which is as below proves the successful synthesis of copolymer.[11]

3. Result and discussion:

Fig.5(A) shows FTIR of soyabean oil and Fig.5(B) shows FTIR of Epoxydized soyabean oil. Peaks near 810 cm⁻¹ confirms epoxidation of soyabean oil in fig.5(B), which is missing in Fig.5(A).

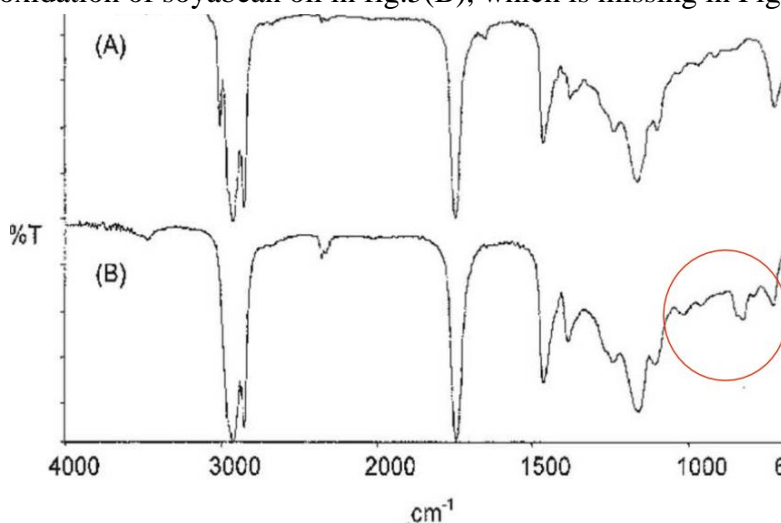


Fig 5.(A)FTIR Soyabean Oil (B) FTIR Epoxydized Soyabean oil

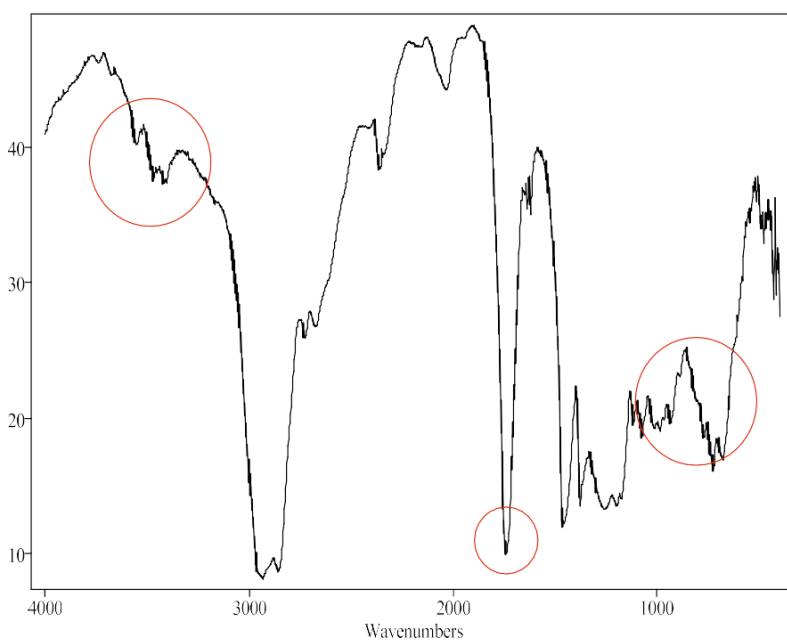


Fig.6 AESBO FTIR

From FTIR as seen in fig.6, a peak at around 3350-3500 cm^{-1} indicates presence of -OH groups due to the addition of the acrylic acid with the opening of epoxy rings in ESBO. Peak near 1720 cm^{-1} confirms esterification of ESBO with acrylic acid and few small peaks around 810 indicate the presence of an epoxy group in ESBO. So, from above FTIR we can say that ESBO was partially Acrylate.

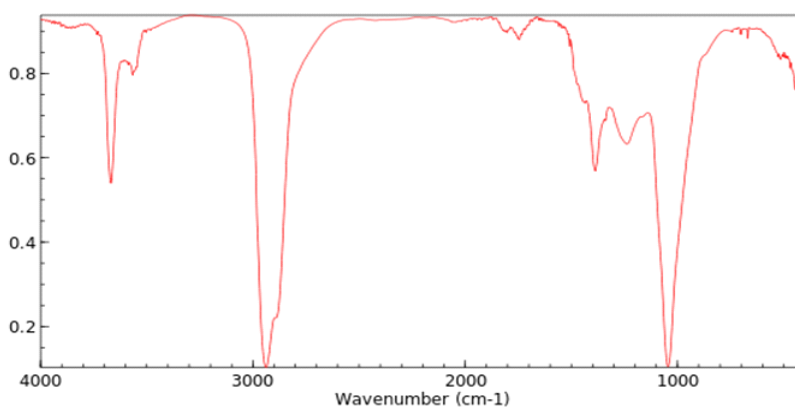


Fig.7 1,4 Butane diol FTIR

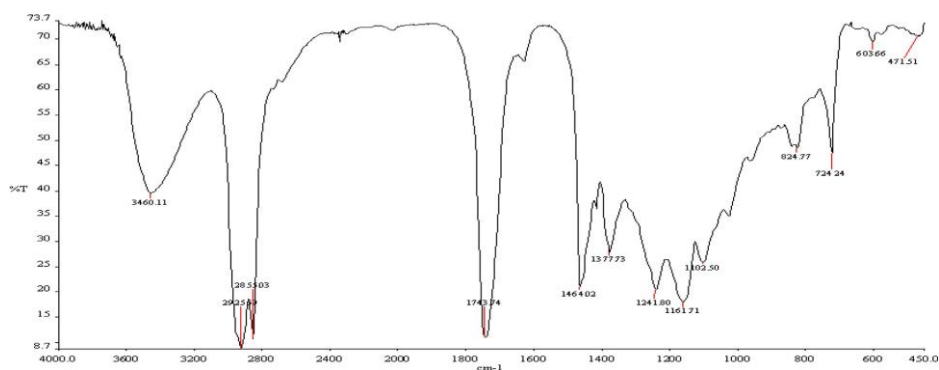


Fig.8 1,4 Butane diol diacetate FTIR

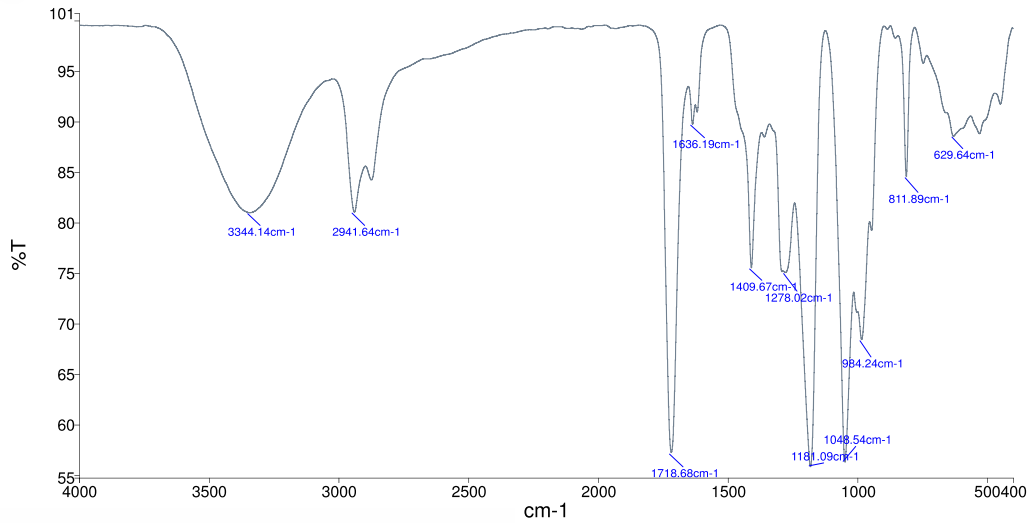


Fig.9 Acrylated butanediol FTIR

In fig 7 peak near 3500 cm^{-1} indicates presence of $-\text{OH}$ group which is absent in fig.8. In Fig 8 peak near 1720 cm^{-1} indicates presence of $-\text{C}=\text{O}$ group while reacted with acetic acid [12]. As per fig – 9 strong peaks at 1718 indicates esterification of butane diol with acrylic acid. Peak at 1636 indicates presence of $\text{C}=\text{C}$ unsaturated group.

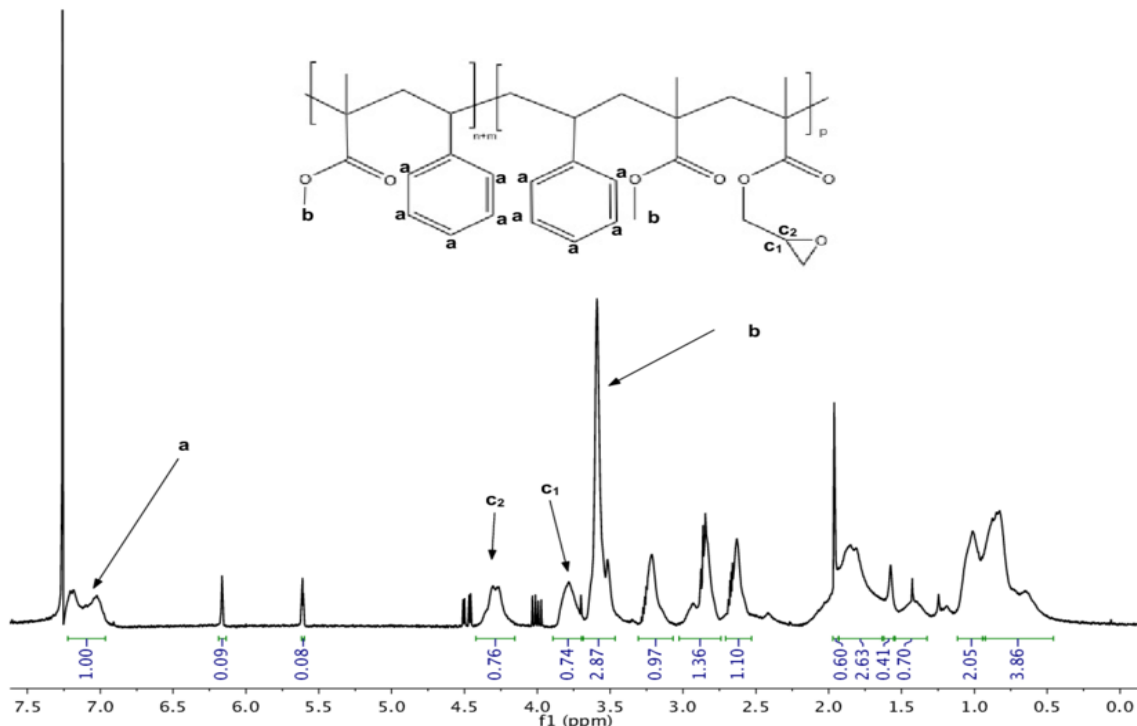


Fig.10 NMR COPOLYMER (Styrene, Methyl methacrylate and Glycidyl methacrylate)

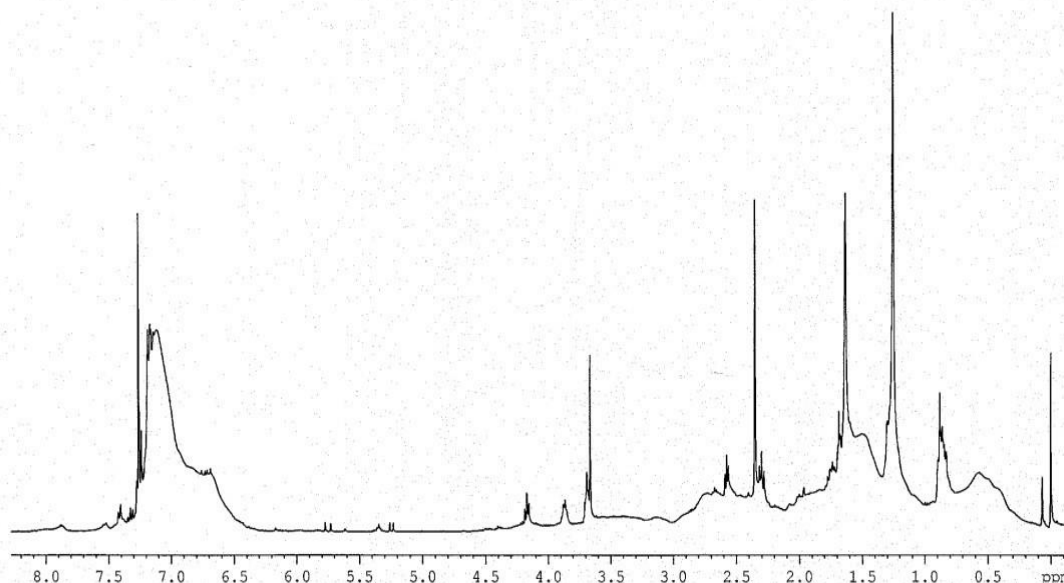


Fig.11 NMR COPOLYMER (Styrene, AESBO, Glycidyl methacrylate, methyl methacrylate and n butyl methacrylate)

As per fig.10 peak at 2.8 ppm to 3.2 ppm appears for epoxy group in NMR spectrum which is disappeared here in fig.11 and eventually new signals around 5.8 ppm to 6.5 ppm appeared which were attributed to the protons of acrylate esters on its chain confirming modification after acrylation. The vinylic hydrogens were detected at around 5.2–5.5 ppm.[13]

As appear in reference fig -11 signals at 6.8 to 7.3 which is also appears in fig 10 corresponding to aromatic ring protons of styrene. Peaks in region 3.4 ppm to 3.75 ppm belongs to methoxy protons of methyl methacrylate. Peaks in region 3.8 to 4.3 ppm belong to methylene proton of glycidyl group of glycidyl methacrylate [14]. Peaks at 1.75 ppm to 1.98 ppm suggest the presence of an epoxy functional group of glycidyl methacrylate.

4. Conclusion

Multifunctional chain extenders are widely used to improved properties of polymers. It is observed that the polyesters like PLA, PBAT, PBS, PBST etc. have tendency of undergoes degradation may be hydrolytic degradation of biopolymers with time, degradation of post processed polymers and degradation of post-consumer polymers. To retain the properties of such partially degraded polymers, chain extenders made from styrene-acrylic-glycidyl acrylate or methacrylate are available in market e.g. Jouncryl ADR of BASF. Here we have developed multifunctional chain extender with partially acrylated ESBO and n butyl methacrylate with styrene and glycidyl methacrylate. Improvement in properties of polymer and/or degraded polymers with this multifunctional chain extender is subjected to further research.

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