

**PARAHYDROGEN-ENHANCED METABOLIC
SPECTROSCOPY AND IMAGING: SYNTHESIS OF VINYL
ESTERS OF ALPHA-KETOCARBOXYLIC ACIDS,
INCLUDING VINYL PYRUTE WITH EXCEPTIONALLY
MILD AND HIGH YEILDING PROPERTIES**

P Venkataramana Reddy, Research Scholar, Department of Chemistry ,
J.S University, Shikohabad, U.P.

Dr. Amit Kumar Chaturvedi , Professor ,Supervisor, Department of
Chemistry, J.S University, Shikohabad, U.P.

Abstract:

These days, fiber reinforced polymer composites have many more useful applications than metals and alloys. Several studies have been conducted to improve the inherent mechanical and thermal properties of composite materials, especially when paired with sustainable, biodegradable, recyclable, and ecologically friendly reinforcements. In recent years, scientists from all around the world have been experimenting with incorporating organic fillers or nanoparticles into the polymer matrix. Because many filler-based composites outperform other neat polymers in terms of mechanical, thermal stability, electrical, optical, and wear resistance, researchers are interested in this study. Material selection is critical to the success of any engineering design that aims to provide a sustainable product at a fair cost. The physical and metaphysical characteristics of the products are just as important as their technological aspects in guaranteeing customer satisfaction. A greater emphasis has been placed on product performance, recyclability, and design in light of these technical considerations. The mechanical and thermal characteristics of reinforced vinyl ester composites with biofillers—date, polyalthia longifolia, and tamarind seed filler—are investigated in this thesis. The bio fillers reinforced vinyl ester composites with different filler loadings (5% to 50% wt.%) were made by compression molding. The mechanical (tensile, flexural, impact, and hardness) and thermal (thermo-gravimetric analysis and heat deflection temperature) properties of the tamarind seed filler reinforced vinyl ester composites, the date seed filler reinforced vinyl ester composites, and the polyalthia longifolia seed filler reinforced vinyl ester composites have all been

investigated. The water absorption behavior of the composites has also been assessed in compliance with ASTM standards in order to study the water uptake percentage. Furthermore, scanning electron microscopy (SEM) technology was used to thoroughly analyze the fractured surfaces of the biofillers reinforced vinyl ester composite.

1 INTRODUCTION

Polymers and polymeric materials have gained significant attention in science and technology in recent years. These materials have been used more often in recent years. Thus, the term "polymer age" refers to this period. The Greek words poly, which means "many," and meros, which means "parts," are the origin of the term polymer. "Macromolecule, big molecules, or giant molecules" is another term for these molecules. Monomers, which are very tiny molecules, may be joined together to form polymers. "Polymerization" refers to the chemical process by which the tiny monomers combine to form polymers [1]. The polymerization process unites two or more species to create high molecular weight polymer molecules that may facilitate the development of substances like heat, water, ammonia, etc. Natural polymers existed on Earth from the beginning of time. Since proteins, ribonucleic acid (RNA), and deoxyribonucleic acid (DNA) are all polymers, life itself is associated with polymers. These are

necessary for the formation of macromolecules in all known forms of life. Some more naturally occurring polymers include cellulose, starch, lignin, and natural rubber. Among them, certain polymers were used early on by human civilizations to create rudimentary items, such as the play balls used in Mesoamerican games that were constructed of natural rubber. The 1800s saw the beginning of the chemical modification of natural polymers, which resulted in the production of several materials including celluloid, gun cotton, and vulcanized rubber. Synthetic polymers are a vast class of polymers that were produced chemically from monomers via the polymerization process.

Synthetic polymers are the materials of today; they were initially considered technologically and practically useful in the early decades of the twentieth century. It is a fact that chemical processes resulted in the production of synthetic polymers, and there are essentially infinite ways to manufacture

them. The only things limiting it were the rules of chemistry and thermodynamics as well as the inventiveness of the synthetic polymer chemist. Due to these endless possibilities, a wide variety of synthetic polymers have been developed. These polymers may be used in almost every area of human endeavor where contracting matter or physical things is required. The enormous molecular structural flexibility that results from the abundance of synthetic options leads to materials with a very wide range of uses and qualities. Polymers are widely used in everyday life and can be found in a wide range of objects, including but not limited to clothing, personal care products, furniture, electrical and electronic appliances, packaging, utensils, automobile parts, coatings, paints, adhesives, tires, and more. Because they are more widely available and have higher economic value than synthetic polymers, several of the polymeric materials are more significant to contemporary civilization.

Chemists operating in labs from the middle of the nineteenth century have unintentionally created a number of synthetic polymers [2]. Staudinger [3] postulated in 1920 that polymers are really macromolecules, a theory that

gained traction in science throughout the next ten years. By using physicochemical techniques to assess the high molecular weight of rubber, supportive data about the macromolecular idea was acquired. Subsequently, in 1929 or so, Carothers [4] started an experimental model that sought to synthesize polymers with specific structures using well-known organic chemistry chemical reactions. The high molecular weight of these molecules was then confirmed through experimental measurements such as the viscosity of polymer solutions [5].

2 LITREATURE SURVEY

Nowadays, the development of polymer composites reinforced with the bio-waste natural fibers and particles is rapidly growing in the many fields such as, the automotive, aerospace, marine, construction, electronics, sporting goods, appliance, and consumer product industries. These composite materials have attractive in various fields because of their inimitable ability to combine the behaviours of various materials to produce a better performance, easily customized and efficient material systems. Consequently the market for polymer composite reinforced with natural fibers and particles is fast growing and lucrative.

Much number of research works have been carried out by material researchers on the natural fiber and particle reinforced polymer composite and its mechanical properties were characterized based on several conditions. There is a lack of study on the protein based fiber reinforced polymer composites. The protein based fibers are abundantly available in day to day life and used as bio-waste materials. The disposal of these bio waste materials consumes more energy as well as time consuming. At the usual practice, large quantities of bio-waste materials are disposed through landfills. The accumulation of a large amount of bio-waste materials releases hazardous gases on the decomposition, which affects the environment. Therefore, the disposal of bio-waste materials is very essential to create a pollution free environment and ecofriendly nature.

Large biomass, forestry and agricultural residues obtained in nature are widely consumed as a possible source of materials for renewable energy in diverse parts of industry. Numerous plants, crops and husks from agricultural resources are being utilized as a vital basis of feasible natural fillers origin for polymer composite. Research and

development of these biological resources might help the eco-system. A Few years ago, fibers and particles obtained from the renewable sources have been widely utilized in the development of fiber-reinforced polymer composite materials. Due to the awareness of ecological protection and deployment of Eco friendly materials for the greener world, the purpose of bio waste natural fibers and particles as bio based reinforcement agents in the polymer composites are significantly developed. Nowadays, the development of polymer composites reinforced with the bio-waste natural fibers and particles is rapidly growing in the many fields such as, the automotive, aerospace, marine, construction, electronics, sporting goods, appliance, and consumer product industries. These composite materials have attractive in various fields because of their inimitable ability to combine the behaviours of various materials to produce a better performance, easily customized and efficient material systems. Consequently the market for polymer composite reinforced with natural fibers and particles is fast growing and lucrative.

Much number of research works have been carried out by material researchers on the natural fiber and particle

reinforced polymer composite and its mechanical properties were characterized based on several conditions. There is a lack of study on the protein based fiber reinforced polymer composites. The protein based fibers are abundantly available in day to day life and used as bio-waste materials. The disposal of these bio waste materials consumes more energy as well as time consuming. At the usual practice, larger quantities of bio-waste materials are disposed through landfills. The accumulation of a large amount of bio-waste materials releases hazardous gases on the decomposition, which affects the environment. Therefore, the disposal of bio-waste materials is very essential to create a pollution free environment and Eco friendly nature.

3 METHODOLOGY

Chemical and mechanical methods may be used to mix polymers. These mechanical procedures include roll milling, melt mixing, solution blending [4], and latex blending. Copolymerization procedures and the creation of interpenetrating polymer networks are often used to create chemical blends [5].

Polymers stay in the stock as suspended microspheres in this kind of mixing.

Interactions between the absorbed suspending agents and emulsifier molecules and neighboring spheres may be avoided. Following thorough mixing, two distinct polymers [6] with latex mixes are produced.

This technology is often used to polymers that melt processing cannot create. This mixing technique involves dissolving two or more polymers in a single solvent. Solvent evaporation and solution mixing are the two phases involved [7].

The issue of solvent/diluent contamination may be avoided using this mixing technique [8]. Controlling the heat flow, viscosity rate, and shearing rate is essential to prevent polymer deterioration. The polymer components are pushed in between the rollers during this mixing process [9].

Vinyl ester resins are primarily diluted with two kinds of solvents: styrene and methyl methacrylate [11]. It takes a long time to stabilize and purify methyl methacrylate. In contrast to methylmethacrylate, styrene is now readily accessible in pre-purified form, and combining it with vinyl ester resin requires less time to create a homogeneous mixture than does

methylmethacrylate. Styrene, also known as vinyl benzene, works well as a diluent for vinyl ester resins because of this [12].

Vinyl ester resins respond well to benzoyl peroxide as an initiator. Vinyl ester resins are not particularly good at creating films. Benzoyl peroxide is utilized as an initiator together with styrene to solve this issue [13]. %wt./wt. vinyl polymer and styrene are combined to create various compositions. As used here, %wt./wt.

the ratio of solute weight to solvent weight. Unsaturated acids, including acrylic and methacrylic acid, function as a solute in this study, whereas produced epoxy resins based on phosphorus (covered in Chapter II) function as a solvent. Numerous studies have combined polyurethanes and traditional epoxy resin (DGEBA) [14]. An epoxy-polyurethane mix is prepared using a crosslinking agent. Diethylene triamine is mostly used as a crosslinking substance. Harani et al.'s [15] modification of epoxy resin to increase fracture toughness included the use of a polyurethane pre-polymer based on hydroxyl-terminated polyester and a chain extender with the polyurethane polymer. It demonstrates an increase in

these systems' impact strength. Phenolic hydroxyl-terminated polyurethane (HTPU) and aromatic amine-terminated polyurethane (ATPU) were used to modify epoxy resin. HTPU-modified epoxy resin has superior fracture toughness compared to ATPU. According to Hsieh and Han [16], grafted IPNs were created by blending polyurethane with epoxy resin using both chemical and physical bonding. They investigated the mechanical characteristics of these systems, which are based on epoxy resin and polyols, and found that the grafted structure significantly improves the tensile strength. Numerous researchers have attempted to enhance the mechanical and physical characteristics of epoxies in the majority of these circumstances. For the purpose of creating epoxy-polyurethane mixtures, a vast amount of information is accessible [17].

4 RESULT & EVALUATION

Polyblends were prepared by means of a solution blending technique. This procedure is often used in the coating industries as well as in the fields of paints, lacquers, and varnishes [18]. The primary rationale for using this technology is its ability to combine materials quickly and thoroughly while consuming little electricity. One of the

main benefits of using diluent styrene is that formulations may be prepared without the requirement for additional solvents such as acetone, tetrahydrofuran, or methyl ethyl ketone. To create a homogeneous mixture, the estimated amounts of styrene (5–10 gms) and benzoyl peroxide were added to the vinyl-ester resin and continuously stirred for 30 minutes using a mechanical stirrer. We very carefully mixed this mixture to prevent the creation of bubbles. Various DGEBA, styrenated vinyl ester resin systems ratios were used to create various kinds of polyblends.

The kinds and behaviors of the different components in a blend, their relative qualities, the degree of heterogeneity, the sort of interface that connects the blends' morphology and structure, and other factors are all likely to have an impact on the behavior of polyblends[19]. Many economically successful goods may be made by using the right proportions. Understanding the behavior of the constituent polymers is crucial for the processing of polyblend.

Phase separation is not seen in any of the suitable polymers. Phase separation was not seen when DGEBA and styrenated vinyl ester resins were thoroughly mixed in solution. As a result,

there is miscibility between the two polymers. Additionally, they complement one another [19]. The kinds of unsaturated acids—acrylic and methacrylic acid, for example—that were used to create vinyl ester resins, as well as the temperature, humidity, and catalyst utilized in the process all affect how quickly the curing process proceeds. Blends were used to make casted films by using diethylenetriamine (DETA) as a crosslinking agent. The ability of vinyl ester resins to create films is poor. This is the reason DGEBA resin was mixed with these resins. Polyblends will provide items that are naturally flame-retardant. The amine present in these curing events caused the epoxy ring to expand up, resulting in the creation of the hydroxyl group (-OH). The following describes how epoxy resins and vinyl ester mixes cure.

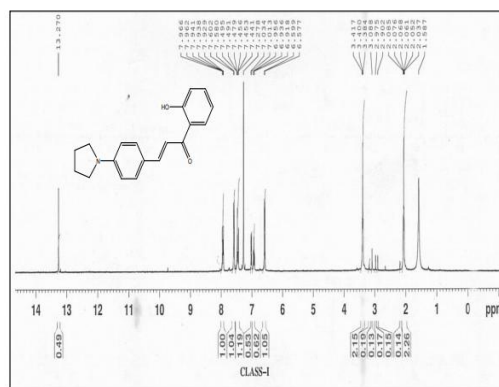


Fig 1 : Because of its basic properties, ketocarboxylic (1) are "privileged building blocks"

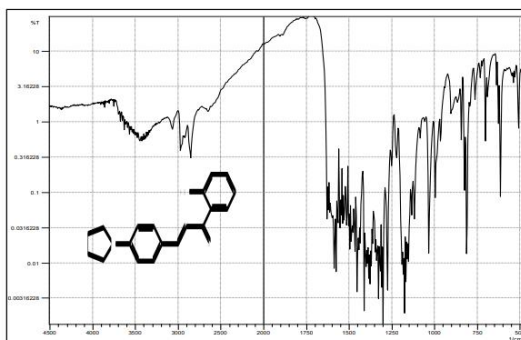


Fig 2: Ketocarboxylic(1) are "privileged building blocks" that, because of their simple

5 CONCLUSION

The utilization of bio-waste chicken feather fibers as reinforcing materials allowed for the study of the mechanical characteristics of vinyl ester composites. The findings demonstrate that as the fiber content of CFF rose from 10 weight percent to 40 weight percent, the mechanical characteristics of the composite increased linearly and thereafter decreased for all instances of fiber lengths. The CFFs with a 40 weight percent fiber content and a 6 mm fiber length were found to be the most appropriate for achieving the optimal blend of mechanical qualities. In every instance of fiber length, there was a negligible increase in the strength value from one weight % to the next. Naturally occurring renewable fiber and particles must meet the following criteria in order to be considered an

appropriate reinforcement material: they must improve the interfacial adhesion between reinforcements and the polymer resin matrix, increase the mechanical properties of the resin matrix, and surpass the critical weight percentage of reinforcement.

6 REFERENCE

1. Alonso, F.; Beletskaya, I.P.; Yus, M. Transition-metal-catalyzed addition of heteroatom-hydrogen bonds to alkynes. *Chem. Rev.* 2004, 104, 3079–3159. [CrossRef] [PubMed]
2. Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. Catalytic Markovnikov and anti-Markovnikov functionalization of alkenes and alkynes: Recent developments and trends. *Angew. Chem. Int. Ed.* 2004, 43, 3368–3398. [CrossRef] [PubMed]
3. Patil, N.T.; Kavthe, R.D.; Shinde, V.S. Transition metal-catalyzed addition of C-, N- and O-nucleophiles to unactivated C–C multiple bonds. *Tetrahedron* 2012, 68, 8079–8146. [CrossRef]
4. Hintermann, L. Recent developments in metal-catalyzed additions of oxygen nucleophiles to alkenes and alkynes. *Top. Organomet. Chem.* 2010, 31, 123–155.
5. Bruneau, C. Group 8 metals-catalyzed O–H bond addition to unsaturated

- molecules. *Top. Organomet. Chem.* 2013, 43, 203–230.
6. Abbiati, G.; Beccalli, E.M.; Rossi, E. Groups 9 and 10 metals-catalyzed O-H bond addition to unsaturated molecules. *Top. Organomet. Chem.* 2013, 43, 231–290.
7. Rao, Y.S. Recent advances in the chemistry of unsaturated lactones. *Chem. Rev.* 1976, 76, 625–694. [CrossRef]
8. Laduwahetty, T. Saturated and unsaturated lactones. *Contemp. Org. Synth.* 1995, 2, 133–149. [CrossRef]
9. Libiszewska, K. Lactones as biologically active compounds. *Biotechnol. Food Sci.* 2011, 75, 45–53.
10. Janecki, T. (Ed.) *Natural Lactones and Lactams: Synthesis, Occurrence and Biological Activity*; Wiley-VCH: Weinheim, Germany, 2013; ISBN 9783527334148.
11. Neatu, F.; Toullec, P.Y.; Michelet, V.; Pârvulescu, V.I. Heterogeneous Au and Rh catalysts for the cycloisomerization reactions of γ -acetylenic carboxylic acids. *Pure Appl. Chem.* 2009, 81, 2387–2396. [CrossRef]
12. Bruneau, C.; Neveux, M.; Kabouche, Z.; Ruppin, C.; Dixneuf, P.H. Ruthenium-catalyzed additions to alkynes: Synthesis of activated esters and their use in acylation reactions. *Synlett* 1991, 11, 755–763. [CrossRef]
13. Kumar, M.; Bagchi, S.; Sharma, A. The first vinyl acetate mediated organocatalytic transesterification of phenols: A step towards sustainability. *New J. Chem.* 2015, 39, 8329–8336. [CrossRef]
14. Liu, X.; Coutelier, O.; Harrison, S.; Tassaing, T.; Marty, J.-D.; Destarac, M. Enhanced solubility of polyvinyl esters in *scCO*₂ by means of vinyl trifluorobutyrate monomer. *ACS Macro Lett.* 2015, 4, 89–93. [CrossRef]