A New Method For The Preparation Of Isocyanate Amino Acid Nanostructure Polymer Composites With An Enhanced Property

Rajesh B. Shingote[a], Bhupesh K. Sharma[a], Narendra S Sonawane[b], Pundalik P. Mali[b], Vikas Patil[c]

a. Shri Jagdish Prasad Jhabarmal Tibrewala University Vidyanagari, Jhunjhunu Churu Road, Chudela, District - Jhunjhunu Rajasthan - 333010
b. B.S.S.P. Mandal's Arts, Commerce & Science College Songir, Dhule, 424002 Maharashtra (India).
c. University Institute of Chemical Technology, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon-425001 India.

Abstract

The present study demonstrates that amino acids and isocyanate form a cross-linked polymer network at room temperature. The amine group in the amino acid acts as a hardener during curing. These results offer several possibilities for applications in important fields that require thermoset materials with toughness, stiffness, and other coating properties. The composites exhibit effective antifungal and positive antibacterial activity against certain strains. TY-TDI and TH-IPDA composites show a significant zone of inhibition compared to standard Amoxicillin. The scanning electron microscopy analysis confirmed the successful formation of the nanocomposites. The synthesized nanocomposites show improvements in characteristics like pencil hardness, scratch resistance, gloss, cross-cut adhesion, and flexibility. Finally, the execution of a chemical reaction between two phase materials was utilized as a modified coating. This chemically activated nanocomposite was integrated into the core structure of the polymer matrix to deliver better surface and mechanical properties.

Keywords: Amino acid, cross-linked, thermal stability, isocyanates, antimicrobial

1. Introduction

In recent years, there has been a growing interest in using renewable resources and bio-based epoxy and isocyanate resins to minimize carbon dioxide emissions that cause global warming and ensure biocompatibility [1]–[4] Chitin and chitosan nanofibers (ChNF and CsNF) are becoming increasingly popular as reinforcing fibres for bio-based polymers due to their biocompatibility, biodegradability, and non-toxic properties [5]–[7] Recently, literature found that reported the thermal and mechanical properties of SPE resins cured with polyamines containing chitosan powder (CsP) and their bio composites, in regard to bio-based epoxy resin/CHNF bio-composites [8]. Wang and Yang, along have recently published a study on the thermal and mechanical properties of composites made from DGEBA, DETDA, and ChNF. Atay et al. have published findings on the self-healing properties of a composite material made from DGEBA, triethylenetetramine, and chitosan powders. However, before curing, most polyamines are toxic. Sometimes adduct types of amines are used to reduce toxicity. The toxicity caused by incomplete consumption of hardeners cannot be completely avoided, leading to hazards from residual hardeners [9]–[11]. The utilization of inorganic nanomaterials as fillers in polymer/inorganic composites has gained interest due to their unique properties. These materials have multiple potential applications in various industries including automotive, aerospace, construction, and electronics. Furthermore, most of the research has been concentrated on polymer nanocomposites derived from natural layered materials, such as montmorillonite, or synthetic clay [12]–[14] The clay minerals have poor electrical and thermal conductivity. To address these limitations, polymer nanocomposites have been enhanced with carbon-based nanofillers like carbon black, EG, CNT, and CNF [15], [16].

The literature found that, hybrid composite material has been developed by combining the properties of both organic and inorganic compounds. Before combining two different chemical species, synergy was achieved through the functionalization of a crucial component. Functionalization enables chemical reactions, resulting in improved mechanical, thermal, electrical, UV resistance, and abrasion properties in hybrid organic-inorganic materials. In polymer nanocomposites, filler materials are exfoliated into the complex matrix due to a lack of covalent interactions. This issue can be addressed by functionalizing the chemicals and covalently bonding the nanostructure fillers to the polymeric matrix. The isocyanate can be combined with chemically modified filler material to enhance the properties of the composite material for application. As a result of using the hydroxyl and acid functionality of the filler, the final composite material exhibits reduced hydrophilic properties. It also forms new hydrophobic amide and carbamate ester linkages [16]–[18]

Polymer isocyanates of solvent based, and water-based emulsion Polymer Isocyanate adhesives were developed in Japan by Kuraray Co., Ltd, Koyo Sango Co., Ltd and Asahi Plywood Co., Ltd in the early 1970's. [19]. The driving forces behind this initiative were to create new markets for poly (vinyl alcohol) and polyethylene chemistry, as well as to develop formaldehyde-free wood adhesives. The original adhesive system consisted of an aqueous

solution of poly (vinyl alcohol) and an isocyanate cross-linker. Further developments using different types of polymer emulsions such as acrylic-styrene (AcSt) poly(vinyl alcohol) (PVA), ethyl(vinyl acetate) (EVAc),, styrene butadiene rubber (SBR) or led to adhesive systems with improved performance. The isocyanate cross-linking agent has been further developed to improve the compatibility and reactivity with the solvent or water-based component. thus several different types are now available for use in emulsion polymer isocyanate adhesive.

Synthetic polymeric scaffolds can be improved by incorporating amino acid moieties into their side chains. This results in several advantages, including a higher level of complexity due to their amphoteric nature, stimuli-responsive properties, chiral recognition, and the ability to undergo self-assembly into secondary and higher-ordered hierarchical structures. Self-assembled supramolecular nanostructures are formed by side-chain amino-acid-based polymers through covalent and noncovalent interactions. These structures can be induced by various external stimuli such as changes in ionic strength, pH, and temperature. A variety of polymeric nanostructures, including vesicles, micelles, toroids, nanogels, nanorods, nanotubes, and nanofibers, can be produced by regulating the conditions under which polymers undergo self-assembly. The properties of polymeric nanostructures can be easily tuned for targeted applications. Numerous articles have been published on the development of polymeric nanostructures derived from amino acids. These structures have shown great potential in various biomedical fields such as drug and gene delivery, antimicrobial activity, antifouling coating, wound healing technology, coating industries and tissue engineering [20]–[23] In this research, here amino acids are organic compounds that contain an amino group (-NH$_2$), carboxylic group (-COOH) and a side chain (R group), which varies among different amino acids. On other hand, Isocyanates are chemical compounds that contain isocyanate group (-NCO), commonly used in the production of polyurethane foams, coatings, adhesives and more. When combining isocyanates with amino acids it refers to formation of urea. Polyurea is a new subset of polyurethane materials formed from poly-isocyanates and amines. In general, polyurea are categorized as heterochain macromolecular compounds because of the presence of the urea linkage -NH-CO-NH- in their structure. Polyurea has significant polarity and due to the polar functional groups can be used as adhesives to bind materials. Such as urea, ester, ether linkages, and even highly reactive isocyanate groups in the molecular structures. In the present work we have prepared urea composite from various amino acids and isocyanates. The product is characterized by thermal gravimetric analysis (TGA) and Differential scanning calorimeter (DSC).

2. Materials and methods

2.1. Materials

Amino acids Serine (CAS No.56-45-1), Tyrosine (CAS No.60-18-4) and Threonine (CAS Amino acids Serine (CAS No.56-45-1), Tyrosine (CAS No.60-18-4) and Threonine (CAS No.72-19-3) purchased from Avra Synthesis Pvt. Ltd. . Toluene 2,4 diisocyanate (CAS No.584-84-9), 4, 4′ -methylene bis (phenyl isocyanate) (CAS No.98101-68-8), Isophorane Diisocyanate

(CAS No.4098-71-9) were purchased from S.D Fine Chem. Ltd., Mumbai, India and used without further purification.

2.2. Methods

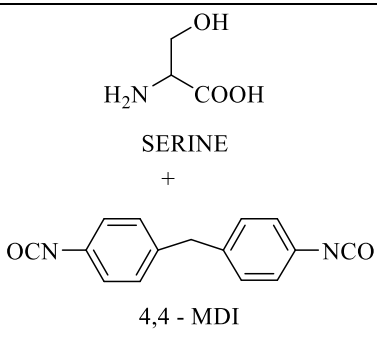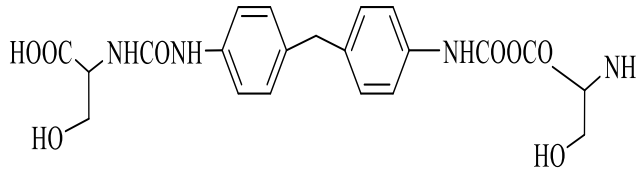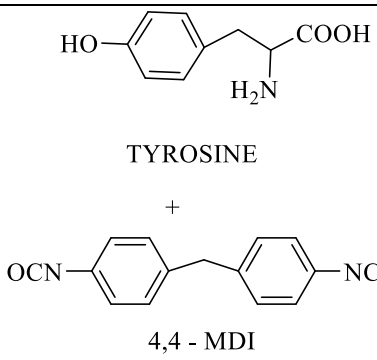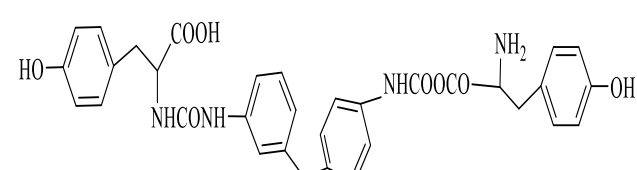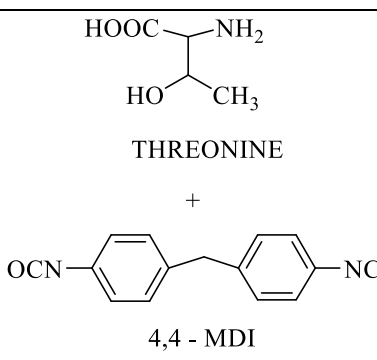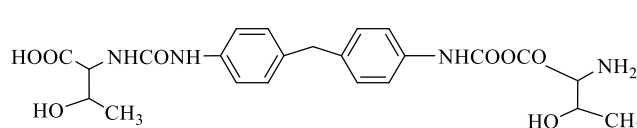Fourier transform infra-red (IR) spectra in the region 4,000–400 cm^{-1} were taken on Shimadzu FTIR 8400 spectrometer. The thermal behavior of prepared composites was performed by thermogravimetric analyzer (Shimadzu, USA thermal analyzer) in the range of 25–600 °C temperature at a heating rate of 10°C/min in N2 inert atmosphere. Differential scanning colorimetry analysis was performed using DSC 7020 (HITACHI) instrument. For DSC analysis, The sample was placed in an aluminum pan, sealed, and equilibrated at 25°C. It was then heated at a rate of 10°C/min under a nitrogen atmosphere to 300°C. The antimicrobial activity of the amino acid-isocyanates composite was performed as per the disc diffusion method. All the necessary microorganisms were obtained from the National Collection of Industrial Microorganisms (NCIM) and the National Chemical Laboratory in Pune, India. The media required for the analysis is purchase from HiMedia Laboratories Private Limited 23, Vadhani Industrial Estate, L.B.S. Marg, Mumbai. The mechanical properties of all amino acid-isocyanate composite samples were tested using various methods, including the Pencil Hardness test according to ASTM D3363, Scratch resistance as per ASTM D7027-13, Gloss Test, flexibility test, and Crosscut adhesion test.
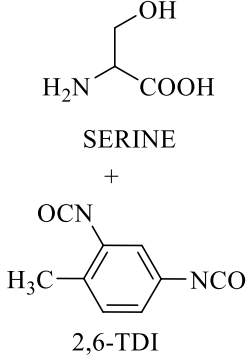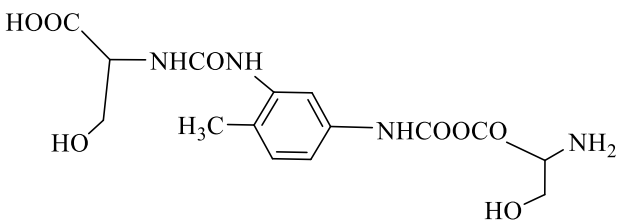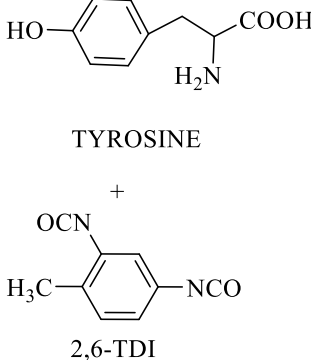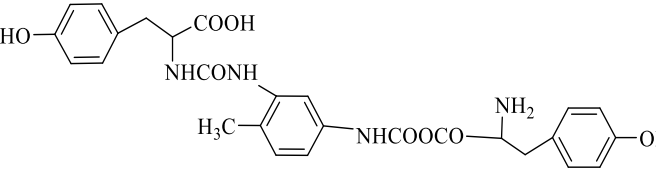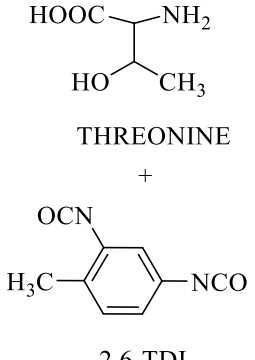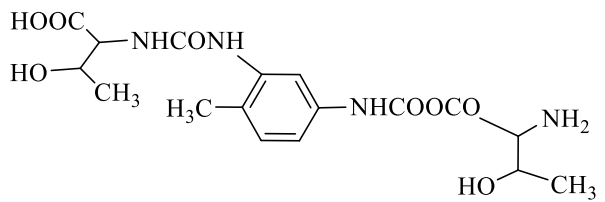
3. Experimental Section
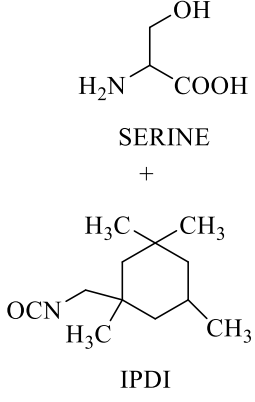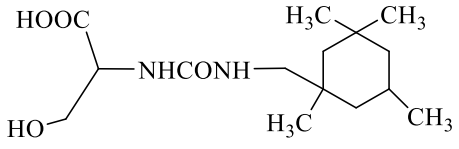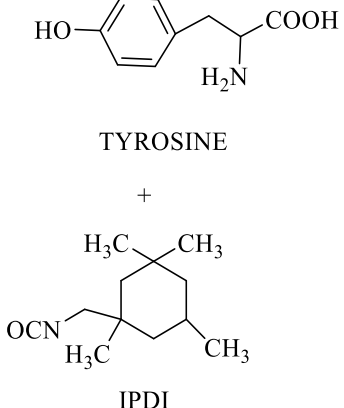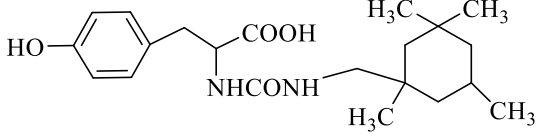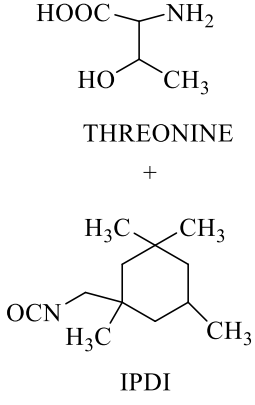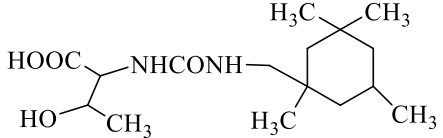
a) Synthesis of Composites from Amino acids-Isocyanates

For the synthesis of composites amino acid (1.5 mole of each amino acid) was combined with desired diisocyanate (1.5 mole) was separately added (dropwise) to amino acids over 30-45 min at 45-50°C under nitrogen atmosphere. The mixture was cooled to room temperature. This amino acid-isocyanate mixture   A series of composites was prepared by three amino acids named Serine (SY), Tyrosine (TY), and Threonine (TH) with three diisocyanates such as 4,4'-Methylene diphenyl diisocyanate (MDI), 2,6-Toluene diisocyanate, (TDI), Isophorone diisocyanate (IPDI) are listed in **Table 1.**

Table 1: Synthesis of Amino Acids-Isocyanates Composites

Sr No.	Code	Chemical reaction	Product
1	SY-MDI	SERINE + 4,4 - MDI	
2	TY-MDI	TYROSINE + 4,4 - MDI	
3	TH-MDI	THREONINE + 4,4 - MDI	

4	SY-TDI	SERINE + 2,6-TDI	
5	TY-TDI	TYROSINE + 2,6-TDI	
6	TH-TDI	THREONINE + 2,6-TDI	

7	SY-IPDI	SERINE + IPDI	
8	TY-IPDI	TYROSINE + IPDI	
9	TH-IPDI	THREONINE + IPDI	

4. Results and discussion:

4.1 FTIR Spectra of composites:

Figure. 1 represents FTIR spectra of amino acid and isocyanates composites. The bands appear at 2900 to 2950 cm^{-1} is due to –CH$_2$ symmetric and asymmetric stretching. The absorption band occurred at 1740 cm^{-1} shows C=O group of carbonyl ester while the C-O bending vibration was observed at 1220-1240cm^{-1}. Absorption band of C=O for urea groups appeared between 1650- 1700 cm^{-1}. Further absorption appeared at 3300, 3330 and 3370 cm^{-1}

corresponding to the stretching vibrations of primary (-NH$_2$). The band appears between 3400 to 3500 cm^{-1} due to the presence of hydroxyl group.
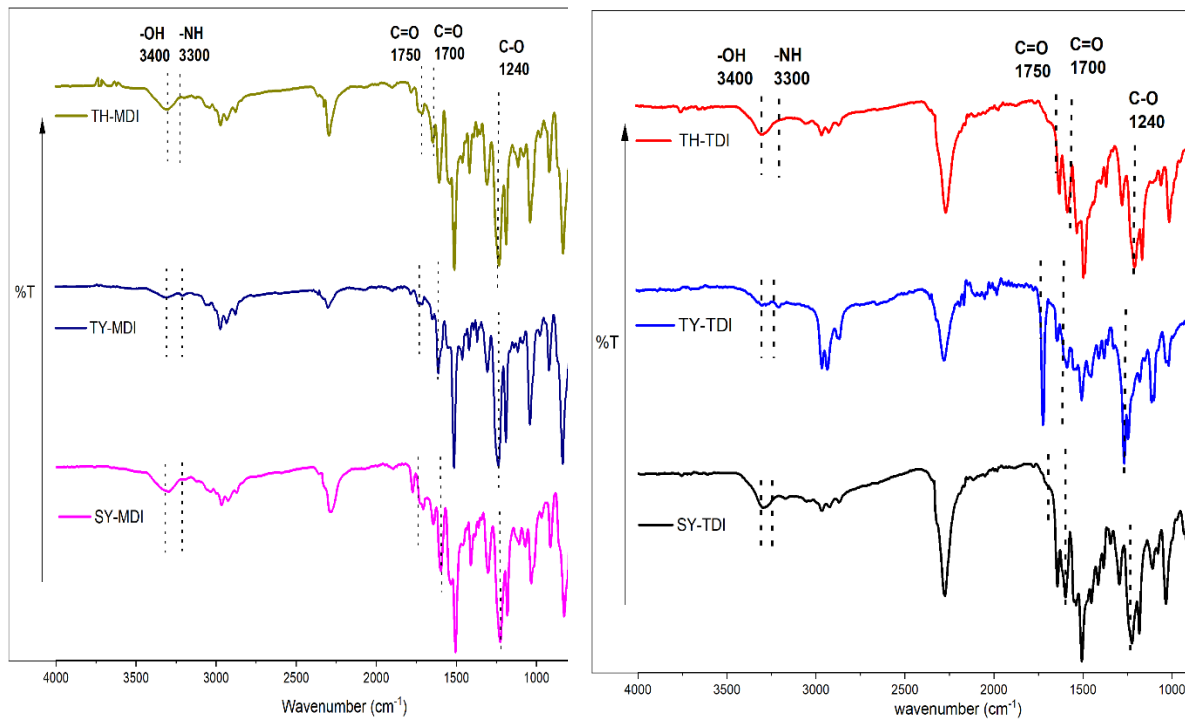
(a)

(b)
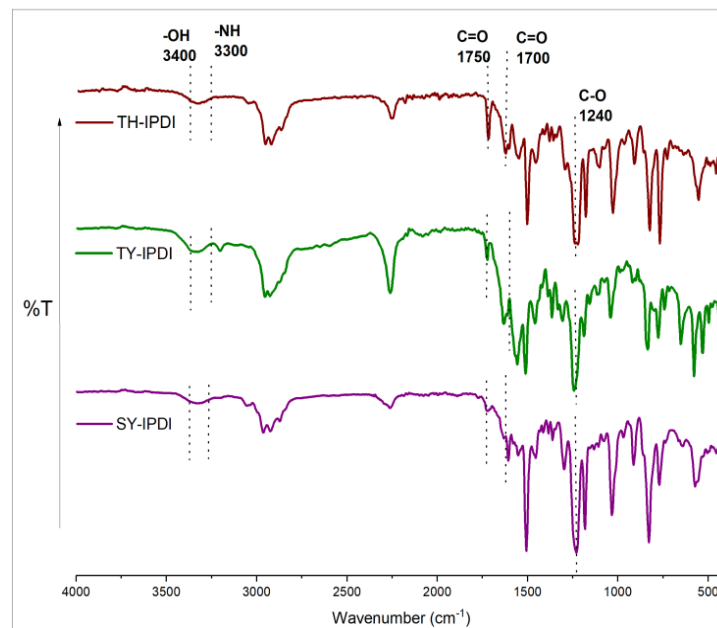
(c)

Fig. 1. IR Spectra of Amino acid and Isocyanate composites: IR spectra of Amino acids (Serine, Tyrocine and Threonine) with a) 4,4'-Methylene diphenyl diisocyanate (MDI), b) Tolylene 2,4diisocyanate (TDI) and c) Isophorone diisocyanate (IPDI).

4.2 Thermal analysis of Composite -

The thermal behavior of composites was determined by the thermogravimetric analysis technique. **Figure 2** shows the thermal behavior of amino acid and isocyanates composites. All the TGA curves of composites showed three steps of thermal degradation. In the first step, degradation of all the composites were started in the temperature range of 220–280°C and ended at 320-340°C with degradation result of 13-30% weight losses due to breaking of urea linkage. In the second step, degradation was observed in the range of 350-365°C and ended at 445-465°C with weight losses of 12-38% due to degradation of ester group. The third step degradation in the range of 460-470°C and ending at 660°C along with weight loss of 14-28% as a result of residual degradation.
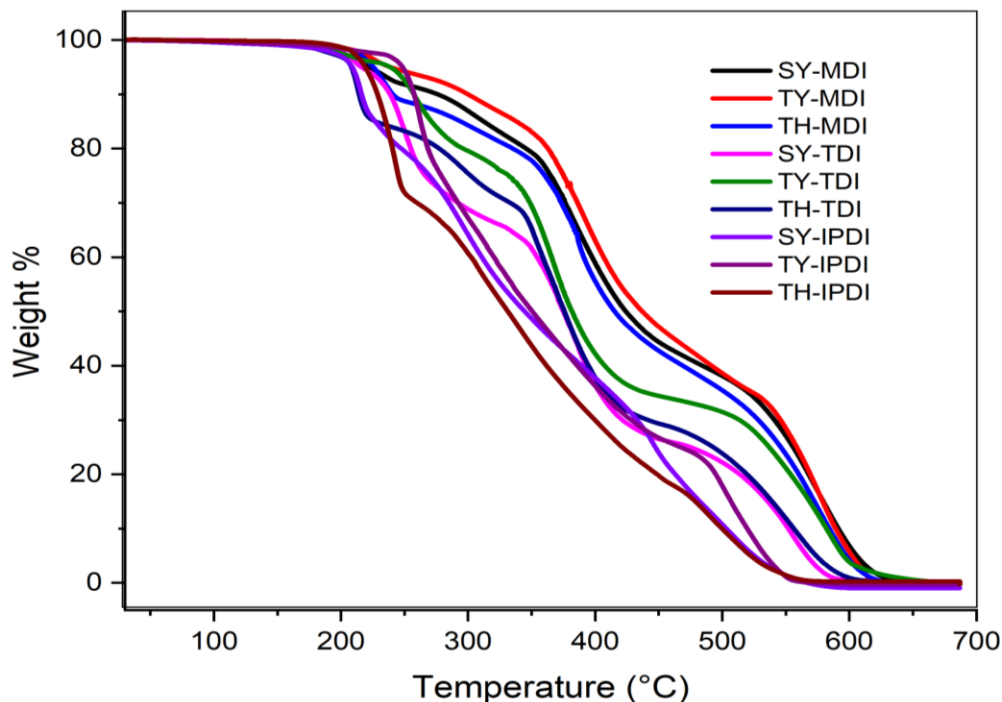
Fig. 2. TGA analysis of Amino acids (Serine, Tyrocine and Threonine) with a) 4,4'-Methylene diphenyl diisocyanate (MDI), b) Tolylene 2,4diisocyanate (TDI) and c) Isophorone diisocyanate (IPDI).

DSC analysis of amino acid and isocyanates composites was performed, and results are shown in **Figure 3**. Initially, an endotherm was observed SY-MDI and TY-IPDI between temperature 25°C–30°C and 150-160°C. Further, an exotherm was observed between 140-150°C and 230-260°C respectively. The thermal behavior of the composite material was studied, and it was observed that all composites exhibited an exothermic peak within the temperature range of 240-260°C. However, after reaching 240°C, a continuous endothermic trend was observed. This behavior was attributed to the release of a water molecule from the composite material.

Fig. 3: DSC analysis of Amino acids (Serine, Tyrocine and Threonine) with a) 4,4'-Methylene diphenyl diisocyanate (MDI), b) Tolylene 2,4diisocyanate (TDI) and c) Isophorone diisocyanate (IPDI)
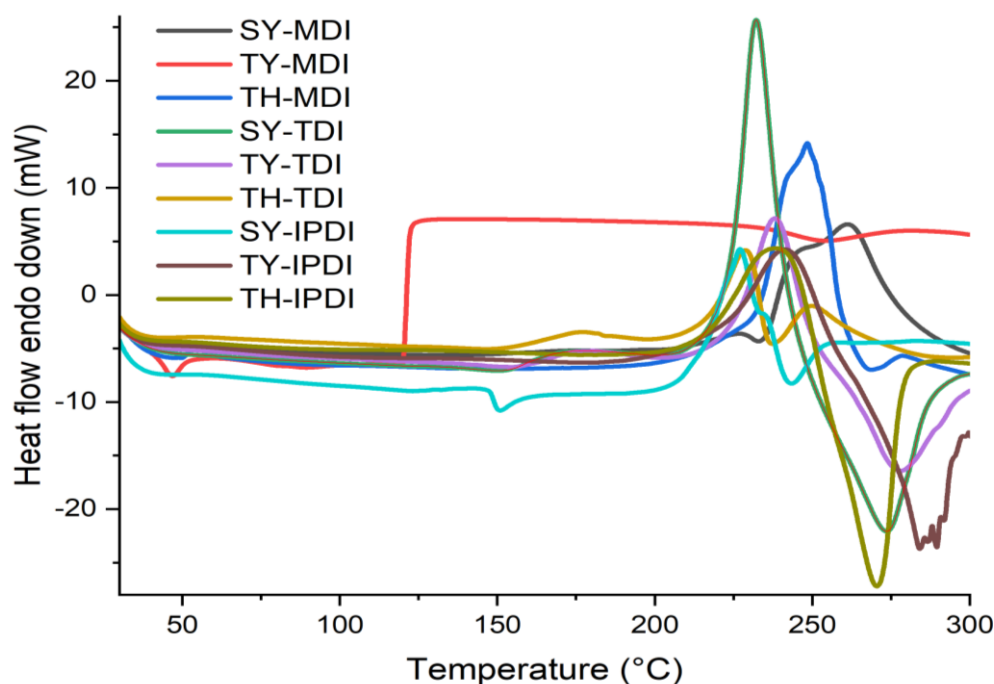
4.3 Evaluation of antimicrobial activity

The biological activity is closely related to various structural parameters, such as chain length, number of functional groups, hydrophilicity, cationicity, hydrophobicity, and other factors. In this paper, we are studying the hydrophobicity of composites made of amino acids and isocyanates. The bi-functional nature of amino acids makes them a key factor in the affinity between synthesized composites and cell membranes. This research explores the use of Serine (SY), Tyrosine (TY) and Threonine (TH) amino acids with three different diisocyanates: 4,4'-Methylene diphenyl diisocyanate (MDI), 2,6-Toluene diisocyanate (TDI) and Isophorone diisocyanate (IPDI) as a template. These amino acids have an asymmetrical sequence and the hydrophobicity of each amino acid has been used to replace the original amino acids at the N-terminus and C-terminus. Recent studies suggest that amino acid composites consisting of epoxy acrylates and isocyanates with a symmetrical sequence of amino acids exhibit improved antibacterial properties. The amino acid composites with symmetrical amino acid sequences were more likely to cause translocation that destroys the cell membrane during interaction with the cell membrane [24].

We have created nine different composites while keeping the active center unchanged. We tested these composites against two types of bacteria and two types of fungi using the disc diffusion method. We observed that the molecular characteristics of these composites were

significantly different from the reference standard. Through this testing, we were able to determine the biological activities of each composite.
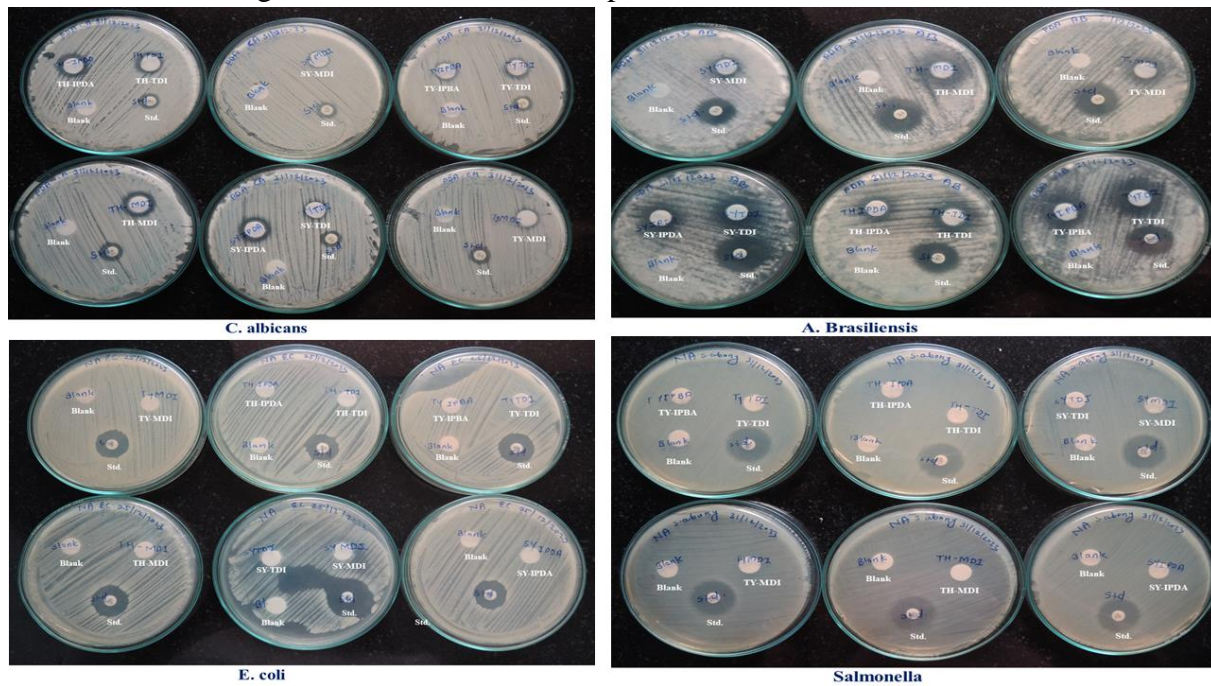
Figure 12. Antimicrobial tests against C. albicans, A. brasiliensis E. coli and Salmonella.

The antimicrobial activity was assessed by agar diffusion assay (disc diffusion method, disc size 6 mm). The microbial tests by disc diffusion assays were performed according to the protocols of Alderman and Smith. Stock solutions [1000 µg/ml] of each compound were prepared in distilled water [25]. The bacteria were cultured on nutrient agar (HiMedia), which is a Soyabean Casein Digest Agar / Columbia Blood Agar base enriched with 5% v/v Sheep/Horse blood. The disc diffusion method provides a quantitative analysis of the effect of bacterial growth in media, as shown in **Fig. 12 and given in Table 2.** The test samples are SY-MDI, TY-MDI, TH-MDI, SY-TDI, TY-TDI, TH-TDI, SY-IPDI, TY-IPDI and TH-IPDI. The results indicate that all composites are effective against fungi C-albicans and A. brasiliensis. In certain instances, they demonstrate stronger values than the typical Amphotericin-B. Additionally, all composites show positive results against Salmonella for their antibacterial activity, except for TH-IPDA. However, both TY-TDI and TH-IPDA composites display a significant zone of inhibition in comparison to the standard Amoxicillin.

4.4 Surface morphology of composites

Morphological SEM analysis of amino acid-isocynate composites involves examining the surface structure and characteristics of the composite material using a scanning electron microscope (SEM).

Table: 2 Disc diffusion assay results of composites

Sr. No.	Compound	C. albicans (mm)	A. Brasiliensis (mm)	E. coli (mm)	Salmonella (mm)
1.	SY-MDI	20	18	-	12
2.	TY-MDI	16	20	-	10
3.	TH-MDI	20	28	-	12
4.	SY-TDI	14	24	-	11
5.	TY-TDI	20	24	12	12
6.	TH-TDI	22	22	-	14
7.	SY-IPDA	20	22	-	12
8.	TY-IPBA	16	22	-	12
9.	TH-IPDA	20	20	12	-
10.	DMSO standard	-	-	No zone of Inhibition	No zone of Inhibition
11.	Amphotericin-B std.	18	26	NA	NA
12.	Amoxicillin std.	NA	NA	30	24
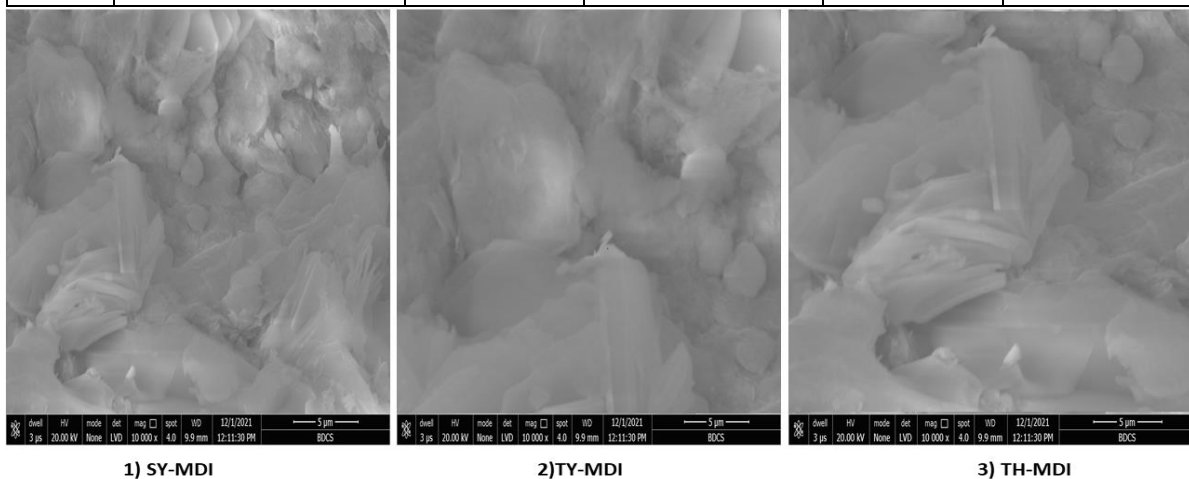
1) SY-MDI   2)TY-MDI   3) TH-MDI

Figure 8. SEM images of serine, tyrosine, and threonine amino acids with isocyanate composites containing Methylene diphenyl diisocyanate (MDI).

The surface structure of the polymer composites samples was carefully analyzed using SEM, and the resulting images are presented in Figure 8. Interestingly, all the composites that were synthesized using serine, tyrosine, and threonine amino acids, in combination with isocyanate containing Methylene diphenyl diisocyanate (MDI), displayed a distinctive spherical shape with a diameter of approximately 5 micrometers. This observation sheds light on the unique characteristics of these composites and highlights their potential for various applications. In the context of MDI, an intriguing observation was made regarding the morphology of threonine amino acids. Specifically, it was noted that the threonine amino acids exhibited a distinct cylindrical-like nanostructure with a diameter measuring less than 12 micrometers. This unique morphology showcases the fascinating properties of threonine amino acids and highlights their potential application in various fields of research and development [26].
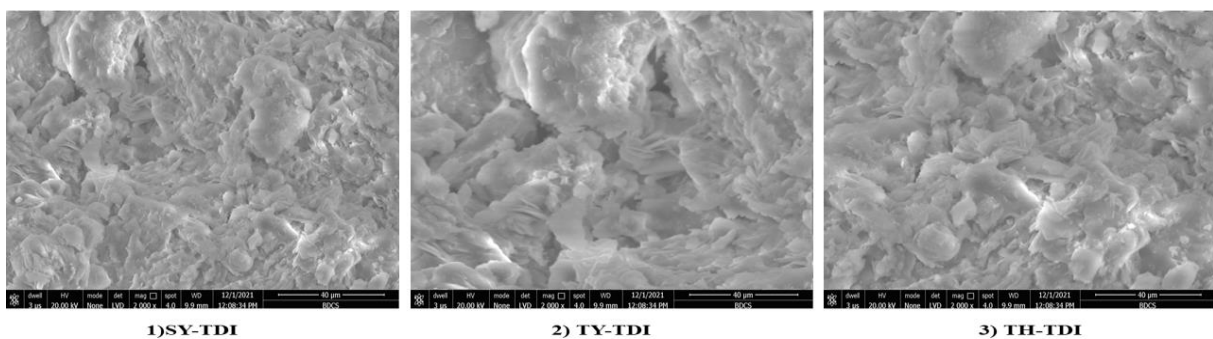
1)SY-TDI   2) TY-TDI   3) TH-TDI
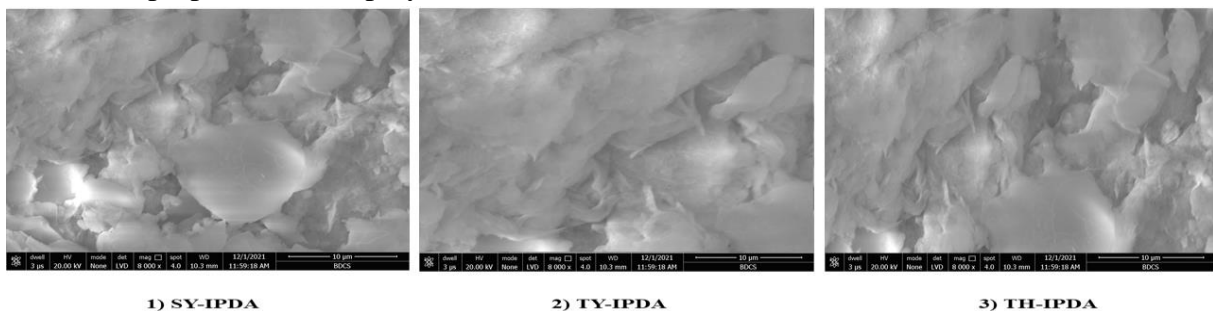
Figure 8. SEM images of serine, tyrosine, and threonine amino acids with isocyanate composites containing 2,6-Toluene di-isocyanate (TDI).

When serine, tyrosine, and threonine amino acids form composites with isocyanate composites consisting of 2,6-Toluene di-isocyanate (TDI), the resulting surface appears to be relatively spheroid in shape, with an approximate diameter of 30-40 µm. The surface texture and shape of these composites can be described as smooth and rounded, resembling small spheres. The results of polymers composites exhibit a nanoscale morphology that is characterized by cylindrical-like shapes with a random in-plane orientation. The results clearly demonstrate the distinctive properties of the polymer structure.

1) SY-IPDA   2) TY-IPDA   3) TH-IPDA

Figure 9. SEM images of serine, tyrosine, and threonine amino acids with isocyanate composites containing Isophorone diisocyanate (IPDI).

The SEM image for the composites of of serine, tyrosine, and threonine amino acids with isocyanate composites containing Isophorone diisocyanate (IPDI) is shown in **Figure 9.** The study reported distinct variations in the structure of serine, tyrosine, and threonine amino acids when combined with Isophorone diisocyanate (IPDI) composites. The analysis revealed the formation of cylindrical-shaped nanostructures with a diameter of less than 10 nm, indicating the unique characteristics of the isocyanate composites.

From the all SEM analysis of composites, it was observed and concluded that the polymers obtained exhibited clear nanoscale morphology, which was evident in their overall composition. The macromolecules showed changes in both shape and size, indicating that they were able to adapt and transform at the nano level. This observation highlights the importance of nanoscale analysis and its ability to detect even the slightest changes in polymers, which can have significant impacts on their physical and chemical properties [27]–[30]

4.5 Mechanical Properties

When examining the mechanical properties of amino acid-isocyanate composites, it is essential to evaluate various characteristics to ensure optimal performance. These characteristics include the Pencil Hardness test, as outlined in the ASTM D3363 standard, which assesses the material's resistance to scratches and abrasions. Additionally, the material's Scratch resistance, as per ASTM D7027-13, should be measured to determine its ability to withstand wear and tear. The Gloss Test evaluates the composite's ability to reflect light, while the flexibility test determines the material's ability to bend and flex without cracking or breaking. Finally, the Crosscut adhesion test, as per ASTM D3359, assesses the strength of the bond between the amino acid-isocyanate composite and the substrate. By examining these characteristics in detail, one can comprehensively understand the composite's mechanical properties and make informed decisions about its potential applications.

The results of all the mechanical tests have been compiled in **Table 3**. The measurement of Pencil hardness is a reliable indicator of a coating's scratch resistance. By utilizing pencils with differing degrees of hardness, the surface of the coating is tested for susceptibility to scratches. The pencil that proves to be the hardest without leaving a mark indicates the level of hardness. Valuable information is gained through this test, revealing the durability of protein epoxy composite coatings and their resistance to abrasion and wear. Scratch testing is a crucial method to determine the maximum stress a material can endure when subjected to bending. Typically, this test involves placing a sample as a beam and applying a load at the center until it reaches a point of fracture. This property is particularly important for applications where the material is exposed to bending forces [31], [32].

Table 3: Mechanical properties of amino acid composite coatings.

Sr. No.	Amino acid composite Coating on MS Panel	Pencil Hardness	Scratch Test (g)	Gloss Test (GU) at 600	Adhesion Test (Crosscut)	Flexibility Test
1	SY-MDI	5H	1400	88	Pass	Pass
2	TY-MDI	5H	1450	91	Pass	Pass
3	TH-MDI	4H	1530	92	Pass	Pass
4	SY-TDI	3H	1400	90	Pass	Pass
5	TY-TDI	5H	1550	94	Pass	Pass
6	TH-TDI	4H	1400	94	Pass	Pass
7	SY-IPDA	2H	1300	93	Pass	Pass
8	TY-IPBA	3H	1350	91	Pass	Pass
9	TH-IPDA	4H	1400	95	Pass	Pass

The gloss test is a crucial aspect when evaluating coatings, as it determines the surface's ability to reflect light evenly in all directions. Gloss meters are widely utilized to measure the gloss of coatings. In the case of all composite's coatings, it is imperative to maintain a consistent gloss level that meets the desired aesthetic standards and remains stable over time. Flexibility testing is an essential evaluation of a coating's durability against deformation, without any cracks or delamination. This assessment is conducted when the coating is exposed to bending or flexing forces, using methods such as the mandrel bend test or conical mandrel bend test. For amino acid-isocyanates composite coatings, it is crucial to maintain a specific level of flexibility, especially if they are applied to substrates that undergo mechanical stress or dimensional changes. Crosscut Adhesion is a term used to describe the ability of a coating to adhere to the surface it is applied to. This property is usually evaluated through adhesion tests, which determine the strength of the bond between the substrate and the coating. These tests are essential to ensure that the coating is durable and long-lasting. When it comes to testing adhesion, crosscutting is a commonly used method. For amino acid composite coatings, achieving strong adhesion is crucial in order to avoid delamination or peeling. To assess the adhesion of the coating, inspect the cut grid and visually examine the amount of coating that has been removed from each square. If necessary, a magnifying glass is recommended to compare the results to a standardized adhesion rating scale. This scale typically ranges from 0 to 5, where 0 indicates no adhesion failure, and 5 indicates complete coating failure.

Conclusion:

The present study demonstrates that amino acids and isocyanate form a cross-linked polymer network at room temperature. The amine group in the amino acid acts as a hardener during curing. These results offer several possibilities for applications in important fields that require

thermoset materials with toughness, stiffness, and other coating properties. The composites exhibit effective antifungal and positive antibacterial activity against certain strains. TY-TDI and TH-IPDA composites show a significant zone of inhibition compared to standard Amoxicillin. The scanning electron microscopy analysis confirmed the successful formation of the nanocomposites. The synthesized nanocomposites show improvements in characteristics like pencil hardness, scratch resistance, gloss, cross-cut adhesion, and flexibility. Finally, the execution of a chemical reaction between two phase materials was utilized as a modified coating. This chemically activated nanocomposite was integrated into the core structure of the polymer matrix to deliver better surface and mechanical properties.

Reference:

[1]   J.-M. Raquez, M. Deléglise, M.-F. Lacrampe, and P. Krawczak, "Thermosetting (bio)materials derived from renewable resources: A critical review," *Prog. Polym. Sci.*, vol. 35, no. 4, pp. 487–509, 2010, doi: https://doi.org/10.1016/j.progpolymsci.2010.01.001.

[2]   E. A. Baroncini, S. Kumar Yadav, G. R. Palmese, and J. F. Stanzione III, "Recent advances in bio-based epoxy resins and bio-based epoxy curing agents," *J. Appl. Polym. Sci.*, vol. 133, no. 45, 2016.

[3]   R. Auvergne, S. Caillol, G. David, B. Boutevin, and J.-P. Pascault, "Biobased thermosetting epoxy: present and future," *Chem. Rev.*, vol. 114, no. 2, pp. 1082–1115, 2014.

[4]   M. M. Reddy, S. Vivekanandhan, M. Misra, S. K. Bhatia, and A. K. Mohanty, "Biobased plastics and bionanocomposites: Current status and future opportunities," *Prog. Polym. Sci.*, vol. 38, no. 10–11, pp. 1653–1689, 2013.

[5]   A. Anitha *et al.*, "Chitin and chitosan in selected biomedical applications," *Prog. Polym. Sci.*, vol. 39, no. 9, pp. 1644–1667, 2014.

[6]   C. K. S. Pillai, W. Paul, and C. P. Sharma, "Chitin and chitosan polymers: Chemistry, solubility and fiber formation," *Prog. Polym. Sci.*, vol. 34, no. 7, pp. 641–678, 2009.

[7]   M. I. Ofem, A. J. Anyandi, and E. B. Ene, "Properties of chitin reinforces composites: a review," *Niger. J. Technol.*, vol. 36, no. 1, pp. 57–71, 2017.

[8]   M. Shibata, M. Enjoji, K. Sakazume, and S. Ifuku, "Bio-based epoxy/chitin nanofiber composites cured with amine-type hardeners containing chitosan," *Carbohydr. Polym.*, vol. 144, pp. 89–97, 2016.

[9]   M. Wang, H. Xue, Z. Feng, B. Cheng, and H. Yang, "Increase of tensile strength and toughness of bio-based diglycidyl ether of bisphenol A with chitin nanowhiskers," *PLoS One*, vol. 12, no. 6, p. e0177673, 2017.

[10]   V. Selvam, M. S. C. Kumara, and M. Vadivel, "Mechanical properties of epoxy/chitosan biocomposites," *Int. J. Chem. Sci*, vol. 11, no. 2, pp. 1103–1109, 2013.

[11]   H. Y. Atay, L. E. Doğan, and E. Çelik, "Investigations of self-Healing property of chitosan-reinforced epoxy dye composite coatings," *J. Mater.*, vol. 2013, pp. 1–7,

2013.

[12] M. Alexandre and P. Dubois, "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials," *Mater. Sci. Eng. R Reports*, vol. 28, no. 1–2, pp. 1–63, 2000.

[13] S. S. Ray and M. Okamoto, "Polymer/layered silicate nanocomposites: a review from preparation to processing," *Prog. Polym. Sci.*, vol. 28, no. 11, pp. 1539–1641, 2003.

[14] Z. Zhang *et al.*, "Partial delamination of the organo-montmorillonite with surfactant containing hydroxyl groups in maleated poly (propylene carbonate)," *Polymer (Guildf).*, vol. 47, no. 26, pp. 8548–8555, 2006.

[15] P. Li, N. H. Kim, S. Bhadra, and J. H. Lee, "Electroresponsive property of novel poly (acrylate-acryloyloxyethyl trimethyl ammonium chloride)/clay nanocomposite hydrogels," *Adv. Mater. Res.*, vol. 79, pp. 2263–2266, 2009.

[16] S. S. Gupta, V. Mishra, M. Das Mukherjee, P. Saini, and K. R. Ranjan, "Amino acid derived biopolymers: Recent advances and biomedical applications," *Int. J. Biol. Macromol.*, vol. 188, pp. 542–567, 2021.

[17] D. S. McLachlan *et al.*, "AC and DC percolative conductivity of single wall carbon nanotube polymer composites," *J. Polym. Sci. Part B Polym. Phys.*, vol. 43, no. 22, pp. 3273–3287, 2005.

[18] Y.-K. Kwon and P. Kim, "Unusually high thermal conductivity in carbon nanotubes," *High Therm. Conduct. Mater.*, pp. 227–265, 2006.

[19] K. Grøstad and A. Pedersen, "Emulsion polymer isocyanates as wood adhesive: a review," *J. Adhes. Sci. Technol.*, vol. 24, no. 8–10, pp. 1357–1381, 2010.

[20] F. Chécot, S. Lecommandoux, Y. Gnanou, and H. Klok, "Water-soluble stimuli-responsive vesicles from peptide-based diblock copolymers," *Angew. Chemie Int. Ed.*, vol. 41, no. 8, pp. 1339–1343, 2002.

[21] D. Schmaljohann, "Thermo-and pH-responsive polymers in drug delivery," *Adv. Drug Deliv. Rev.*, vol. 58, no. 15, pp. 1655–1670, 2006.

[22] Z. Tang *et al.*, "Polymeric nanostructured materials for biomedical applications," *Prog. Polym. Sci.*, vol. 60, pp. 86–128, 2016.

[23] L. Li, K. Raghupathi, C. Song, P. Prasad, and S. Thayumanavan, "Self-assembly of random copolymers," *Chem. Commun.*, vol. 50, no. 88, pp. 13417–13432, 2014.

[24] C. Sun *et al.*, "Antibacterial activity and mechanism of action of bovine lactoferricin derivatives with symmetrical amino acid sequences," *Int. J. Mol. Sci.*, vol. 19, no. 10, p. 2951, 2018.

[25] D. J. Alderman and P. Smith, "Development of draft protocols of standard reference methods for antimicrobial agent susceptibility testing of bacteria associated with fish diseases," *Aquaculture*, vol. 196, no. 3–4, pp. 211–243, 2001.

[26] S. Mallakpour and M. Khani, "Nanostructured amino acid containing poly (amide-imide) s from different diisocyanates: synthesis and morphology properties in molten TBAB as a green media," *Polym. Bull.*, vol. 70, no. 7, pp. 2125–2135, 2013.

[27] A. Abdolmaleki, S. Mallakpour, S. Borandeh, and M. R. Sabzalian, "Fabrication of biodegradable poly (ester-amide) s based on tyrosine natural amino acid," *Amino Acids*, vol. 42, pp. 1997–2007, 2012.

[28] S. Mallakpour and M. Khani, "Novel optically active poly (amide-imide) s derived from N-trimellitylimido-L-isoleucine and different diisocyanates," *Polym. Bull.*, vol. 59, pp. 587–596, 2007.

[29] H. S. Nalwa, *Encyclopedia of nanoscience and nanotechnology (v. 8. Ne-P)*. American scientific publishers, 2004.

[30] W. Jin, "Using bio-chars as potential catalysts for upgrading wood pyrolysis vapors," 2013.

[31] P. Mali, N. Sonawane, V. Patil, R. Mawale, and N. Pawar, "Designing efficient UV-curable flame-retardant and antimicrobial wood coating: Phosphorodiamidate reactive diluent with epoxy acrylate," *J. Polym. Res.*, vol. 28, no. 10, 2021, doi: 10.1007/s10965-021-02722-8.

[32] N. V. Hong *et al.*, "Processing rigid wheat gluten biocomposites for high mechanical performance," *Compos. Part A Appl. Sci. Manuf.*, vol. 79, pp. 74–81, 2015.