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Investigation on Effect of 3-Trimethoxysilyl Propyl Methacrylate based Nano-ZnO/CTF Nanocomposite Hydrogel- Synthesis and Characterization

R. Princy Sowmya [a], **S. Harini** [a], **S. Nikila** [a], **S. Guhanathan** [a, *]

[a] Department of Chemistry, Muthurangam Government Arts College (Autonomous), (Affiliated to Thiruvalluvar University, Serkadu, Vellore-632115), Vellore-632002, Tamil Nadu, India

* Corresponding author Email: sai_gugan@yahoo.com

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Abstract: A groundbreaking method has been developed for the preparation of CTF (citric acid, triethanolamine, and 2-furoic acid) hydrogel that promises significant advancements in material science. By reacting CTF hydrogel with nano-zinc oxide and 3-trimethoxysilyl propyl methacrylate to create a nanocomposite. The hydrogel's properties, meticulously monitored through swelling behavior assessment (a broad pH range from 2.0 to 11.0), strikingly, the swelling percentage was highest in a neutral medium (pH 7.0), outperforming both alkaline and acidic environments. This innovative approach paves the way for swelling behavior of the synthesized hydrogel. The results of swelling equilibrium significantly improve with ascending concentrations of both nano ZnO and TMP respectively. The synthesized CTF- nano ZnO-TMP nanocomposite hydrogels have been characterized using various analytical techniques like UV, FTIR, ^{1}H NMR, ^{13}C NMR, SEM-EDX which confirms the presence of 3-trimethoxysilyl propyl methacrylate (TMP) and nano-zinc oxide in the CTF network. Thermogravimetric analysis (TGA) has also been carried out for the present investigation. The outcome of thermal studies reveals that CTF-Nano-Zn-TMP nanocomposite hydrogels found to have thermally stable to 400 ^{0} C. Hence, the compounds of present investigation may be utilized for high performance applications.

Keywords: Hydrogels, pH Sensitive, Swelling Equilibrium, ZnO Nanocomposites, 3-Trimethoxy Silyl Propyl Methacrylate

1. Introduction

Hydrogels are an innovative class of polymers capable of absorbing water or biological fluids, and expand to several times their original dry volume [1]. Hydrogels are excellent materials because of their high water content, resulting in its flexibility that nearly resembles natural tissue. The most biodegradable substances, which can breaking down without producing hazardous by products, ensuring environmental and human health safety. Furthermore, hydrogels achieve pH neutrality after absorbing water, making them adaptable for a variety of applications. Their ability to successfully rewet is critical, allowing them to discharge or retain absorbed solutions tailored specifically to agricultural or hygienic applications. Hydrogels are an excellent alternative for new solutions in a variety of industries due to their unique combination of features [2].

The cross-linked density and hydration properties are defined specifically by the monomer 3-(trimethoxysilyl) propyl methacrylate (TMP). These carefully selected monomers successfully achieve a balanced hydrophilic-hydrophobic character, appropriate crosslink density, and increased swelling ability in these hydrogels, which are specifically developed for stimuli-responsive release of curative medicines [3]. 3-(Trimethoxysilyl) propyl methacrylate (TMP) was especially chosen as the hydrophobic component due to its favorable siloxane group, which improves effectiveness as well as performance [4]. 3-(Trimethoxysilyl) propyl methacrylate, which comprises tri-alkoxy groups, is used extensively in current clinical dentistry and other technical applications. It utilizes silane coupling agents to successfully improve adhesion between incompatible materials, making it a critical choice for achieving reliable and a long-lasting outcome [5] When copolymerized with other monomers, this substance forms polymer films with greatly improved mechanical characteristics and adhesion to a variety of surfaces. Its potential to improve UV stability makes it appealing, as does its effectiveness as a crosslinking agent in polymer gels. By successfully interacting with functional groups such as hydroxyl and carboxyl groups, it produces stable covalent bonds that strengthen the mechanical performance of polymers. Furthermore, TMP's versatility makes it useful in a variety of disciplines, including lithium-ion batteries, engineering applications, dental restorative materials, and a wide range of biological applications. Using this novel chemical can produce improved outcomes. Nano ZnO composites provide a safe, non-toxic antibacterial solution and are thermally stable, making them a great alternative for a variety of applications [6]. Nano ZnO composites provide a non-toxic alternative with promising applications in a variety of disciplines, including medicine, antimicrobial coatings, ceramics, and mold treatments. Their safety and adaptability distinguish them. Furthermore, thermo-sensitive hydrogels are extraordinary materials that react to small temperature changes by expanding or shrinking. These hydrogels not only have antibacterial capabilities, but they also have excellent thermal stability, making them perfect for novel applications in a variety of industries. Embracing these materials can result in safer and more effective solutions [7]. Nano zinc oxide (ZnO) particles have been widely studied and identified as highly potent antibacterial agents. Their exceptional biocompatibility with mammalian cells strengthens their potential for safe application in different industries, making them a great alternative for enhancing health and safety solutions [8]. Numerous commercial solutions containing nano ZnO particles provide efficient photo protection, maintaining the skin is adequately shielded against dangerous UV radiation [9]. In the present study, we thoroughly investigated the synthesis and characteristics of TMP-ZnO hydrogels by unique CTF (citric acid-triethanolamine-2 furoic acid) framework to improve the molecular structure of nano ZnO and TMP utilizing selective cross-linking. Furthermore, we synthesize and thoroughly describe a hydrogel composite infused with nano ZnO particles, demonstrating the promise of this refined material.

2. Experimental

2.1 Materials

This investigation used citric acid (CA), triethanolamine (TEA), 2-furoic acid (FA), and ethanol were from Sigma-Aldrich in Bangalore, India. The Nano ZnO particles containing 30 – 80 nm as the particle size, were acquired from Ad-Nano Technologies.3-(trimethoxy-silyl)propyl methacrylate (TMP) were obtained from Sigma-Aldrich, India. The chemicals were used in their received state, ensuring their purity without any extra purification steps. Throughout the experiment, we relied on distilled water to maintain consistency and accuracy.

2.2 Method

2.2.1. Preparation of CTF Hydrogel

In this innovative synthesis, we commenced 0.04 mol of citric acid (7.6848 g) dissolved in ethanol and addition of triethanolamine (0.025 mol or 3.3006 g) in a round-bottomed flask with a mechanical stirrer drop wise, the sticky white gel-like, Citric Acid-Triethanolamine (CT) pre-polyester compound were formed. 2-Furoic acid (0.025 mol or 2.802 g) dissolved in ethanol were added to pre-polyester for one hour at 140 °C throughout the reaction. The formation of a glassy brown gel (CTF), confirmed the reaction's success. The resulting gel was soaked in purified ethanol for 24 hours to remove unreacted monomers and then dried in a vacuum oven for another 24 hours.

2.2.2. Preparation of [CTF (ZnO- TMP)] Composites

This preparation set the stage for the next exciting step: adding nano zinc oxide dissolved in ethanol, to the CTF hydrogel compound. In this synthesis, we incorporated 3-(trimethoxy-silyl)propyl methacrylate (TMP) dissolving in ethanol to the CTF-ZnO gel. We successfully synthesized the hydrogel CTF with various nano zinc oxide and TMP ratios to customize its characteristics.

Table 1. The monomer composition utilized for the polymeric hydrogel synthesis

Sl.No	Monomers	Composition
1	Citric acid (CA)	0.040 mol or 7.6848 g
2	Triethanolamine (TEA)	0.025 mol or 3.3006 g
3	2-Furoic acid (FA)	0.025 mol or 2.802 g
4	Nano Zinc oxide (ZnO)	Varying series from 0.5 g, 1.0 g and 2.0 g
5	3-(trimethoxy-silyl)propyl methacrylate (TMP)	Varying series from 0.5 g, 1.0 g and 2.0 g

Table 1 shows detailed experimental data for a series of developed polymeric hydrogels including nano zinc oxide and TMP. Table 1 shows the composition of the monomers employed in the polymeric hydrogel investigations.

2.2.3. UV–Vis Spectrophotometer

The [CTF(ZnO-TMP)] complex was studied using a double-beam UV-vis spectrophotometer. The mixture was sampled at regular intervals to check the reaction completion process. The wavelengths of the samples were obtained between the range of 200 to 400 nm.

2.2.4. Fourier transform infrared (FTIR) spectroscopy analysis

The molecular structure of [CTF(ZnO- TMP)] was efficiently studied using the FTIR Shimadzu 8400S spectrophotometer with samples generated using the standard KBr disc procedure. The spectra were recorded between 500 to 4000 cm^{-1} range.

2.2.5. Swelling behavior

One of the key aspects of water absorption in hydrogels that highlights their exceptional qualities is swelling behavior. At room temperature, the 0.200 g dried hydrogel was submerged in buffer solutions with pH values ranging from 2.0 to 11.0. The swelled hydrogels were periodically taken out of the swelling medium, wiped with filter paper to remove any remaining moisture, weighed, and then put back in the same solution. This meticulous procedure ensuring their capacity to absorb is measured. Lastly, filter paper was used to eliminate the hydrogels surface water. The following formula (1) can be used to measure the effectiveness of water absorption,

$$\boxed{S_{eq}\% = \frac{W_{eq} - W_d}{W_d} \times 100}$$

Where, W_d = Initial weight of the dry hydrogel

W_{eq}= weight of the increased weight of the sample at equilibrium.

2.2.6. ^{13}C NMR and ^{1}H NMR Spectroscopy Analysis

The BRUKER Advance III 400 MHz was used to perform ^{13}C and ^{1}H NMR spectral analyses in order to clarify the structure, and interaction of the molecules. The DMSO as solvent were used in this method.

2.2.7. Scanning electron microscopy (SEM and EDX)

To fully investigate the effects of polymer and crosslinker concentrations on surface morphology, we analyzed the hydrogel [CTF(ZnO-TMP)] using efficient scanning electron microscopy (SEM). This SEM's Energy-Dispersive X-ray spectrometer (EDX) allows for quick and accurate qualitative and quantitative elemental composition analysis, which is crucial for our research.

2.2.8. Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) using an SDT Q 600 Simultaneous TGA (TA Instruments) were used to examine the thermal properties of polymeric hydrogels. TGA curves were recorded in the temperature range of ambient to 500 ^{o}C.

3. Results and Discussion

3.1 UV-Visible spectroscopy

The UV-visible absorption spectrum of nano zinc oxide particle obtained was shown in Figure.1. The UV–visible absorbance of synthesized nano ZnO were measured within 200–400 nm wavelength. Citric acid absorption properties shows minimal absorption within 230 nm [10]. The TEA exhibits a peak absorption at 386 nm. The UV absorption spectrum of 2-furoic acid prominently features absorption at 240 nm and 280 nm, highlighting aromatic structure [11]. The UV absorption spectrum of siliane in TMP is at 200-300 nm range. This is due to the methacrylate group and the conjugation of C=C double bonds, which play a role in absorbing UV light effectively [12].

3.2. Fourier transform infrared (FTIR) spectroscopy analysis

The IR spectrum of [CTF(ZnO- TMP)] hydrogel reveals in (Figure 1) a strong bands at 1073.22 cm^{-1} and 1012.02 cm^{-1} distinctly indicate (Si-O) and C-O-C stretching. Additionally, symmetric stretching vibration of the -C-H bond at 2972.13 cm^{-1}, 884.11cm^{-1}, 761.32cm^{-1} and 669.32cm^{-1}. The prominent peak at 2972.13 cm^{-1} is firmly linked to the stretching vibration of the methylene group within the polymer backbone [13]. The prominent IR band detected in the range of 3364.73 cm^{-1} is a clear indicator of the O–H stretching vibration associated with the carboxylic group found in both citric acid and 2-furoic acid [14]. The C-N absorptions occur prominently at 1294.95 cm^{-1}, highlighting significant molecular interactions. Furthermore, hydrogels exhibit a strong absorption band near 1721.55 cm^{-1}, clearly indicating the presence of C=O stretching of TMP and additional peak was observed at 1176.79 cm^{-1} and 1118.23cm^{-1} shows C–O stretching of ester groups. The new absorption peaks have been identified at 1474.06 cm^{-1} and 1390.64 cm^{-1}, demonstrating a clear stretching of the –COO- group [15] as shown in Figure 2. FTIR curve secondary vibrations of Zn-O bond are found to be lying at 669.32 cm^{-1} [16].

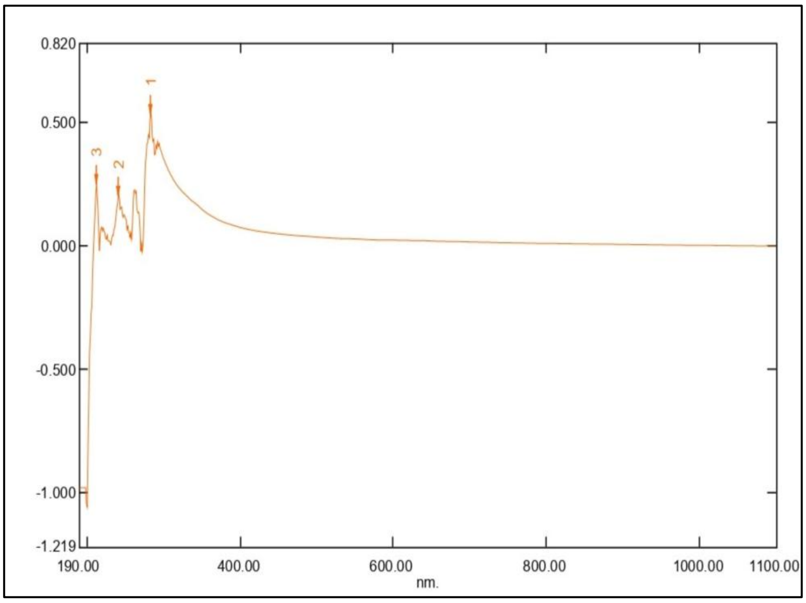

Figure 1. UV Spectrum of [CTF(ZnO- TMP)] polymeric hydrogel

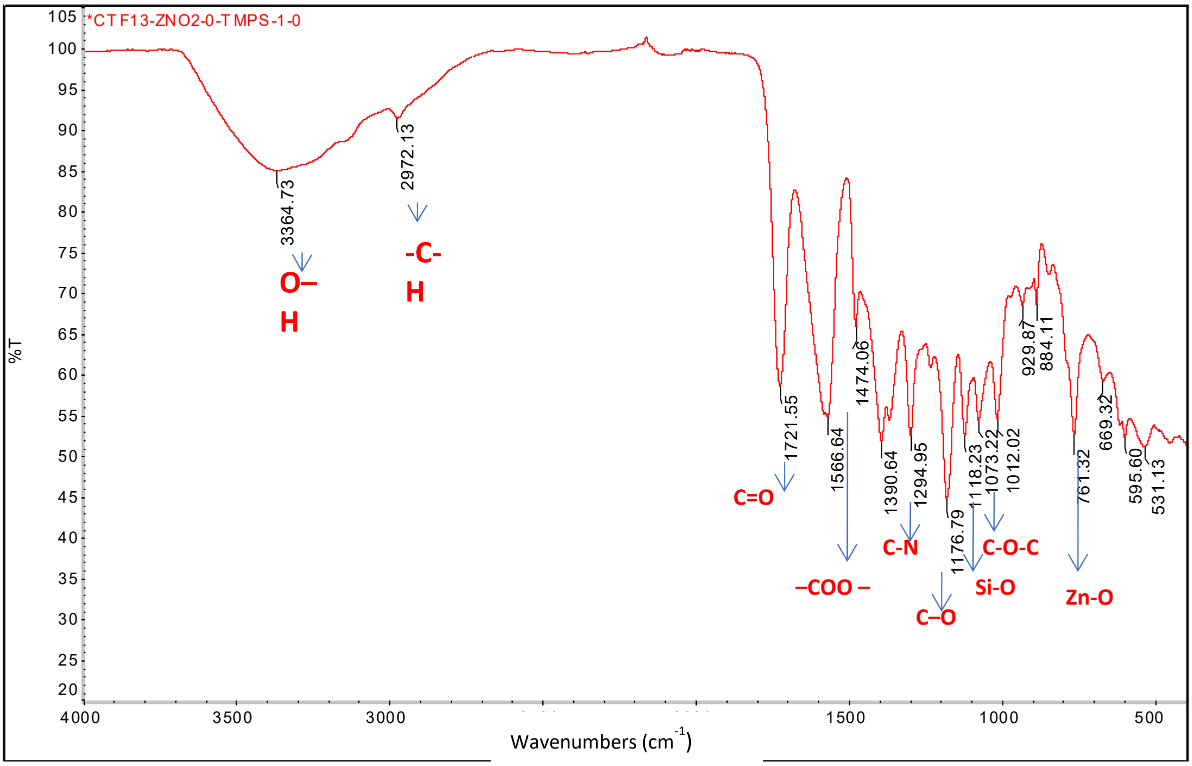

Figure 2. FTIR Spectra of [CTF(ZnO- TMP)] polymeric hydrogel

3.3. Swelling behavior

Figure 3 illustrates the compelling experimental results of swelling equilibrium in hydrogels, showcasing the impact of various pH levels alongside differing proportions of nano ZnO and TMP. The CTF hydrogels, made up of citric acid, triethanolamine, and 2-furoic acid, are strategically combined in a 2:1:1 ratio, with the volume of citric acid significantly surpassing that of triethanolamine and 2-furoic acid. Notably, existing literature indicates that the incorporation of citric acid effectively fine-tunes the swelling equilibrium, underscoring its critical role in optimizing hydrogel performance [17-19]. The series of nine different hydrogels (CTFZT$_1$, CTFZT$_2$, CTFZT$_3$, CTFZT$_4$, CTFZT$_5$, CTFZT$_6$, CTFZT$_7$, CTFZT$_8$ and CTFZT$_9$) showed impressive equilibrium swelling behavior for all samples showcasing maxima at a neutral pH compared to lower and higher pH. The swelling percentage (Seq %) of the CTFZT$_9$ hydrogel varies significantly across different pH levels, was found to have 295 %, 340 %, 380 %, 334 %, and 310 %, respectively is shown in Table 2.

Table 2. The swelling equilibrum percentage of [CTF(ZnO- TMP)] nano composite hydrogel

S.No	Sample code	CA + TEA + FA (in grams)	Nano ZnO (in grams)	TMP (in grams)	Swelling Equilibrum (%) pH 2	4	7	9.2	11
1	CTFZT$_1$	0.400 + 0.200 +0.200	0.5	0.5	115	119	128	118	117
2	CTFZT$_2$			1 .0	120	130	133	128	125
3	CTFZT$_3$			2 .0	130	140	153	136	130
4	CTFZT$_4$	0.400 + 0.200 +0.200	1.0	0.5	130	135	156	137	135
5	CTFZT$_5$			1 .0	143	158	168	160	146
6	CTFZT$_6$			2 .0	166	187	218	180	170
7	CTFZT$_7$	0.400 + 0.200 +0.200	2.0	0.5	245	254	290	257	254
8	CTFZT$_8$			1 .0	265	284	310	290	275
9	CTFZT$_9$			2 .0	295	340	380	334	310

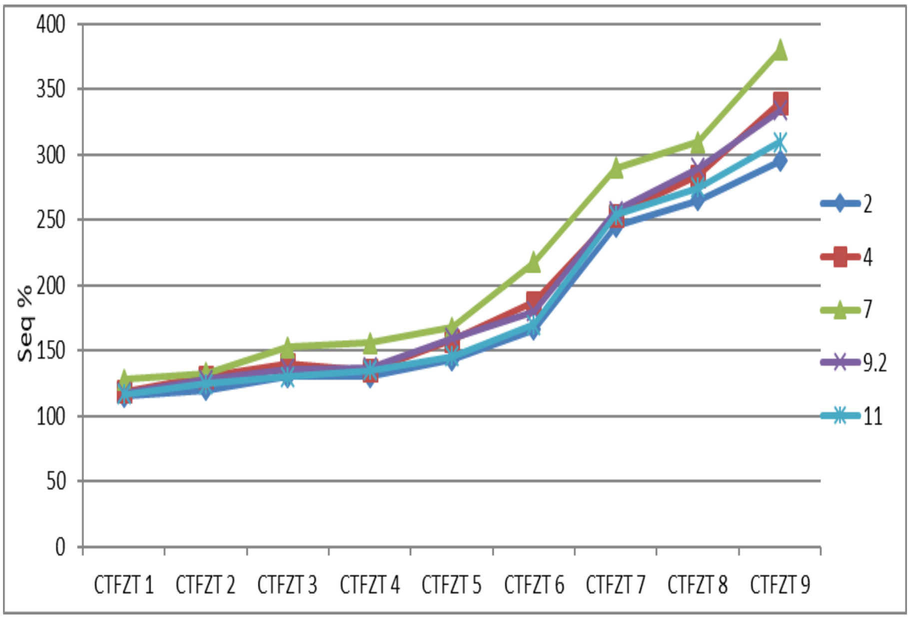

Figure 3. The swelling equilibrum percentage of nano composite hydrogel at varies series of pH ranging (2.0 ,4.0, 7.0, 9.2 and 11.0)

As shown in Figure 3, the hydrogels demonstrates a remarkable increase in swelling ratios from pH 2.0 to pH 7.0, highlighting its effectiveness in neutral environments compared to slightly acidic. However, a dramatic decrease in swelling occurs from pH 7.0 to pH 11.0, emphasizing the importance of pH control in applications. In low pH conditions (pH 2.0), the protonation of anionic carboxylate groups causes the polymeric network to collapse, demonstrating the sensitivity of the hydrogel to acidic conditions. Conversely, the free carboxylic acid groups play a crucial role by promoting dissociation, thereby enhancing the hydrogel's swelling capacity. The distinctive behavior underscores the potential of CTFZT$_9$ hydrogel for targeted applications where pH responsiveness is essential [20, 21]. As the pH rises from 4.0 to 7.0, the carboxylic acid groups undergo ionization, which causes hydrogen bonds to break. This ionization generates repulsive forces between the groups, driving the hydrogel to swell significantly and achieve an enhanced swelling ratio [22, 23].

3.4. ^{1}H NMR and ^{13}C NMR Spectroscopy analysis

The ^{1}H-NMR Spectra of [CTF (ZnO- TMP)] polymeric hydrogel, peak observed around 3.1–3.3 ppm is compelling evidence of the proton signal of –OCH_2–CH– group. Furthermore, the multiple peaks between 2.5 - 3.1 ppm, along with those between 3.8-5.0 ppm, clearly indicate the presence of protons in the –CH_2– group and the alcoholic –OH group found in citric acid. Notably, a significant signal at approximately 3.5 ppm can be attributed to the methoxy groups connected to the siliane atom in TMP. The ester and methyl groups in TMP resonate at 3.8 and 1.2 ppm, respectively, adding to the complexity of the spectrum. Additionally, the prominent peak appears around 6.9 ppm suggests the presence of protons of =C-H [24], while the multiple peaks between 7.0 to7.5 ppm and at 8.0 ppm correspond to the protons in the –CH– group from 2-furoic acid. The absence of the signal at 11 ppm strongly demonstrates that the protons from all three carboxylic units of citric acid, along with the carboxylic proton of furoic acid, were actively consumed during the polyesterification reaction with triethanolamine as in Figure 4. The proton from the methacrylate group appeared in the range of 5.5 to 6.0 ppm as a multiplet due to spin-spin coupling [25]. The aromatic protons in 2-furoic acid was observed at 7.5 – 8.5 ppm due to their electronegative oxygen in the furan ring [26]. The –CH_2– group adjacent to the hydroxyl group appears as multiplets in the range of 3.2–3.5 ppm in TEA, due to the splitting of protons [27].

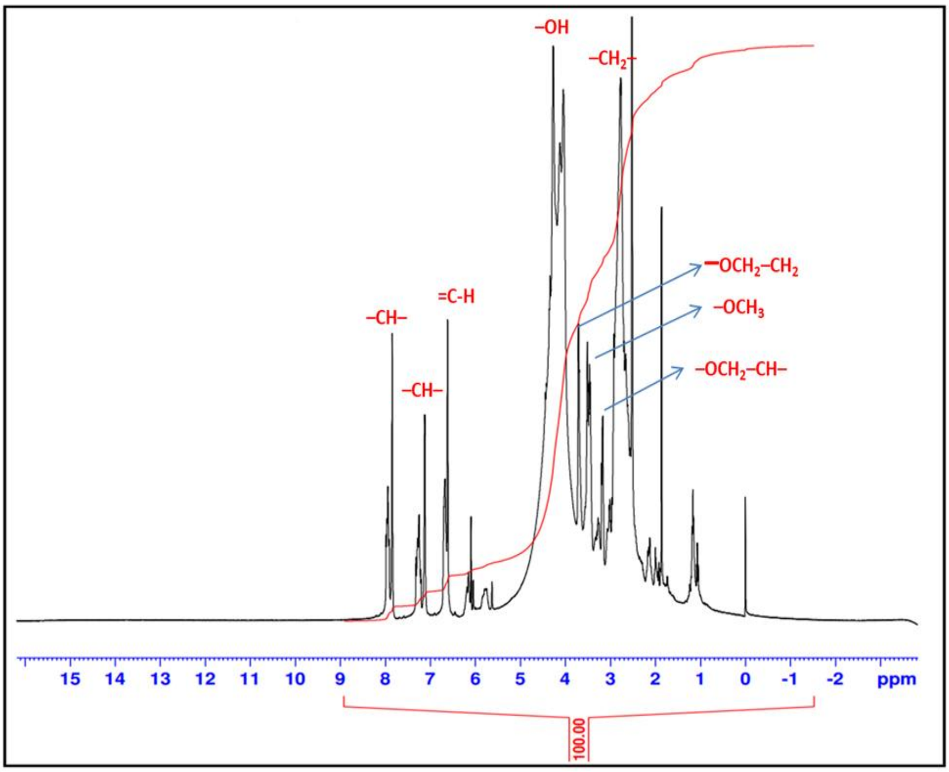

Figure 4. The ^{1}H-NMR Spectra of [CTF (ZnO- TMP)] polymeric hydrogel

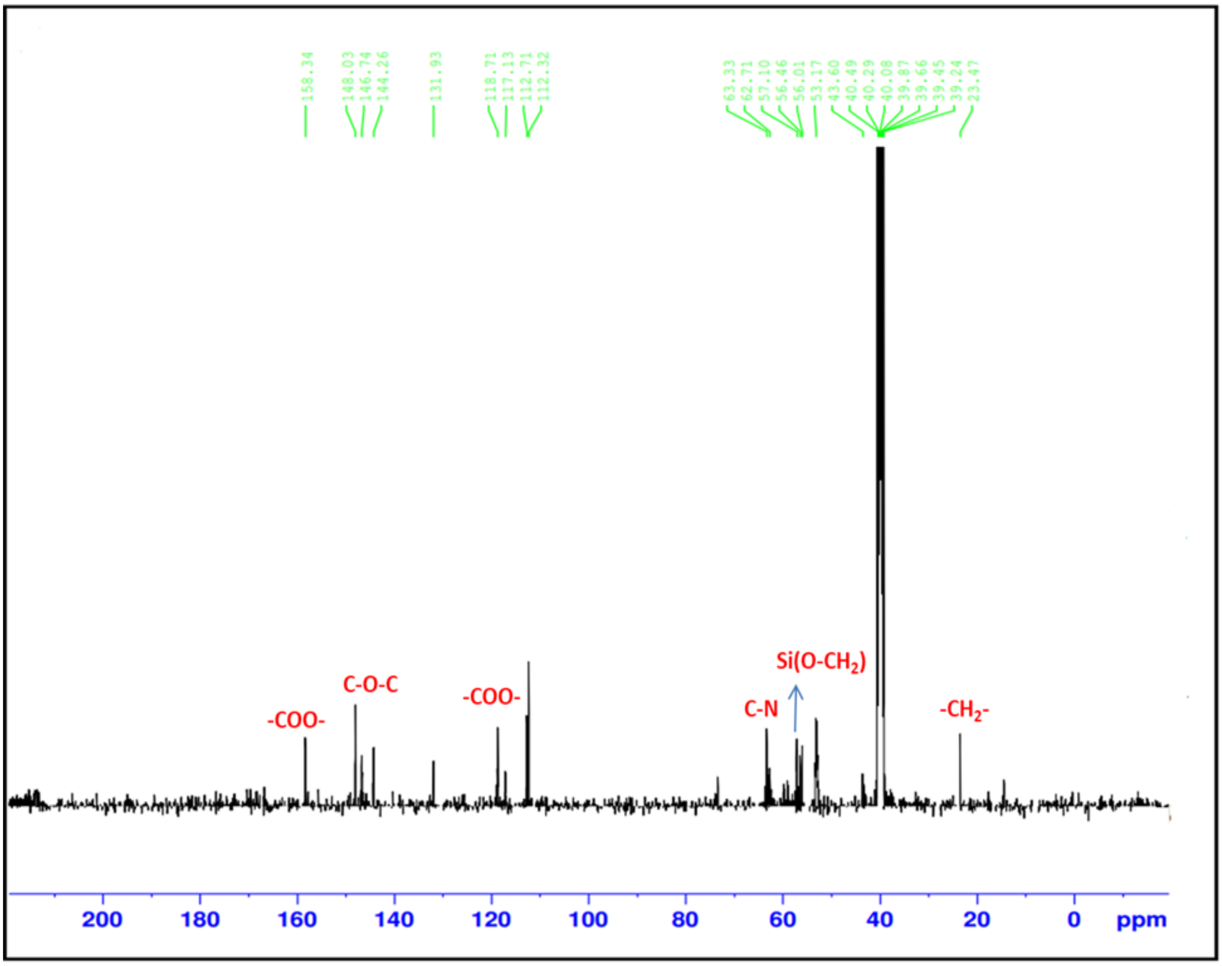

Figure 5. The 13C-NMR Spectra of [CTF (ZnO- TMP)] polymeric hydrogel

In Figure 5, the analysis of ^{13}C NMR clearly highlights significant signals that reveal crucial insights into the [CTF(ZnO- TMP)] molecular structure. The prominent signals at 56.01 ppm and 56.46 ppm are indicative of the 3-trimethoxysilyl group, while the 23.47 ppm signal demonstrates the presence of -CH$_2$- in TMP. Moreover, the peaks at 43.60 ppm and 57.01 ppm confirm the -CH$_2$- groups found in Citric acid and Triethanolamine, respectively, showcasing the diverse interactions within the compounds. Furthermore, the signals ranging from 63.33 ppm and ester components containing methylene carbon at 62.71 ppm represent the carbon atoms in the C-N and -CO-O-CH$_2$-CH$_2$- structure of TEA integral to the polyester network. The signals between 39.87 ppm and 40.08 ppm are a clear indication of DMSO's presence [28]. Notably, the aromatic carbon of furoic acid is represented by a signal at 118 ppm, and a C-O-C ring structure found during polyesterification is seen at 146.74 ppm. The peak at 158.34 ppm strongly suggests the formation of an ester carbonyl from furoic acid.

3.5. Scanning electron microscopy (SEM and EDX)

The scanning electron microscopy (SEM) technique is broadly used to confirm the surface morphology, size and shape nature of materials. It can be seen from Figure 6 (a,b) that pure [CTF(ZnO- TMP)] hydrogel has been exhibited a characteristic three-dimensional uneven spongy, roughness and cavity structures. This is because of the presence of the hydrogen bonded network and ideal homogeneity among the constituents [29]. It seems that nano ZnO particles of almost grain and flower shapes are accumulated on the surface of hydrogels. It also shows in EDX that the smaller nano ZnO particles distributed throughout the hydrogel network. SEM with EDX confirmed the presence of nano ZnO particles in the nanocomposite hydrogel. In order to confirm the formation of [CTF(ZnO- TMP)] complex, EDX analysis was performed. During the EDX measurement, different areas were focused and the corresponding peaks are shown in Figure 7. Both ZnO and Si can be seen in the synthesized composite structure in the EDX spectrum.

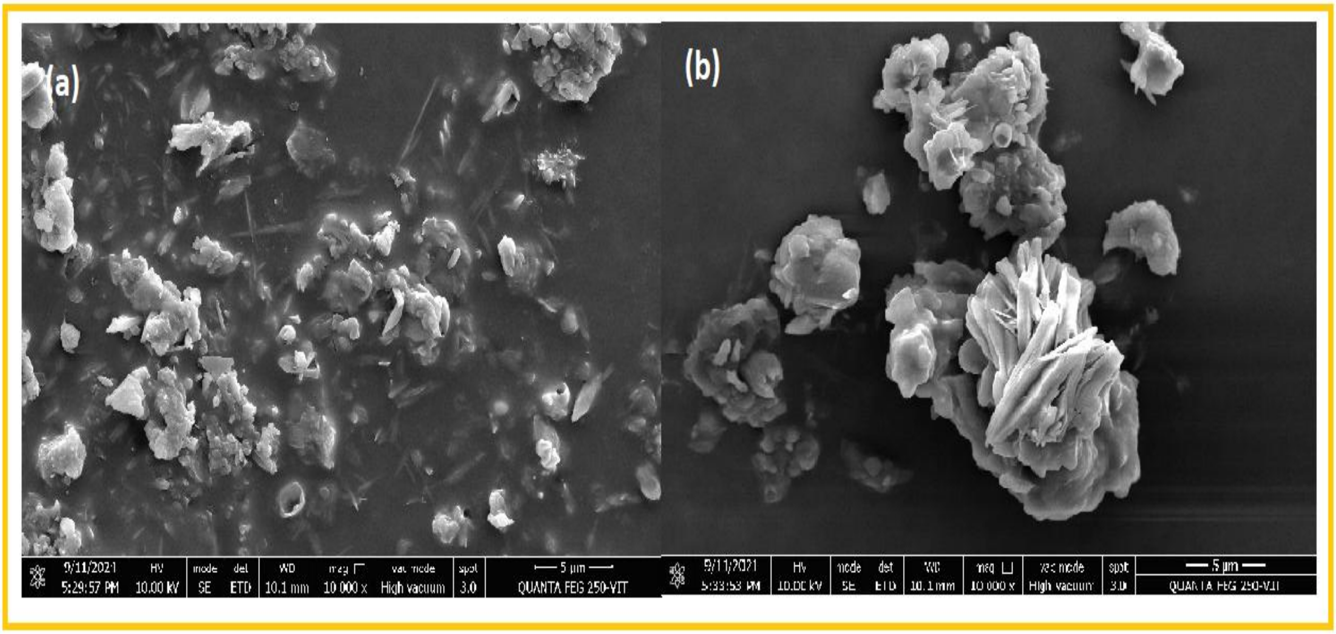

Figure 6. SEM image of [CTF (ZnO- TMP)] polymeric hydrogel

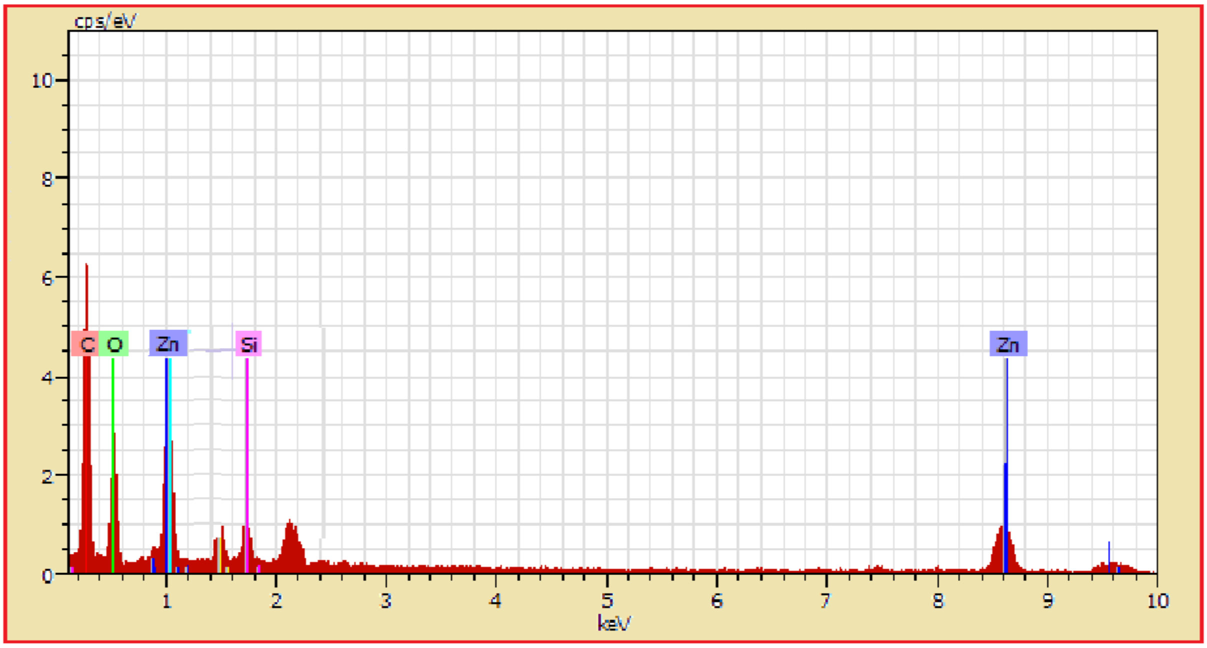

Figure 7. The SEM-EDX of [CTF (ZnO- TMP)] polymeric hydrogel

Table 3. EDX weight ratio of [CTF(ZnO- TMP)] polymeric hydrogel

Sl. No	Elements	Weight (%)	Atomic (%)
1	Carbon	56.67	66.99
2	Oxygen	32.78	29.09
3	Zinc	2.32	1.39
4	Silyl	1.12	0.59

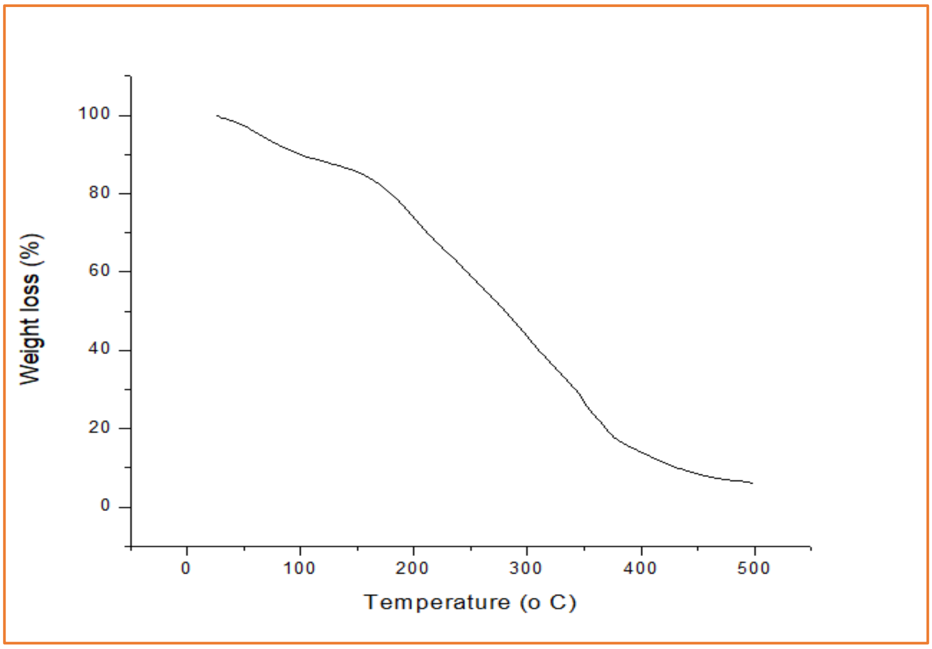

Figure 8. The TGA of [CTF (ZnO- TMP)] polymeric hydrogel

The quantity of C, O, Zn and Si were 56.67 %, 32.78 %, 2.32 % and 1.12 % measured in weight percentage respectively. While the 66.99 %, 29.09 %, 1.39 % and 0.59 % is the atomic weight of C, O, Zn and Si respectively as shown in Table 3.

3.6 Thermal Characterization of Polymeric Hydrogels

Figure 8, effectively showcases the thermogram characteristics of the polymer hydrogels of [CTF(ZnO-TMP)] complex. The analysis of thermal stability across different hydrogels was conducted by evaluated weight loss within the temperature range from 0°C to 500 °C. As depicted in Figure 8, the hydrogel demonstrates distinct degradation events. The initial stage occurs between 50 °C and 150 °C, where a weight loss of 9 % is observed, corresponds to the fragmentation of CH_2CH_2OH. The subsequent weight loss stage, occurs between 350 °C and 450 °C, resulting in a weight loss of 78 %, which could be loss of linked carboxylate 2-furoic acid of the polymeric materials.

4. Conclusions

In this study, the polymeric pH-responsive citric acid-based hydrogels with varying nano ZnO and TMP with triethanolaine and 2-furoic acid were synthesized. The UV analysis the presence of nano ZnO in the [CTF(ZnO- TMP)] complex polymeric hydrogel. The FTIR spectroscopy confirms the formation and structure of hydrogels by the formation of C–O stretching of ester groups, Si-O (1073.22 cm^{-1}), C-O-C(1012.02 cm^{-1}), Zn-O(669.32 cm^{-1}). Swelling results of hydrogel were also studied at various pH 2.0–11.0 revealed that swelling and swelling equilibrium were higher in neutral (pH 7) medium. Swelling clearly prove that citric acid has a capacity to tune the swelling behavior. Moreover, the high amount of nano ZnO and TMP ($CTFZT_9$) yields the large swelling ratio compared to that of other hydrogel compounds. The ^{1}H-NMR Spectra of [CTF(ZnO- TMP)] polymeric hydrogel, peak observed around 3.1–3.3 ppm proton signal of $–OCH_2–CH–$ group and 3.5 ppm methoxy groups of silicon atom in TMP. The ester and methyl groups in TMP peak at 3.8 and 1.2 ppm, is observed. The ^{13}C-NMR signals at 56.01 ppm and 56.46 ppm are indicative of the 3-trimethoxysilyl group, the aromatic carbon of furoic acid is at 118 ppm, and a C-O-C polyesterification is seen at 146.74 ppm, similarly the peak at 158.34 ppm suggests the formation of an ester carbonyl from furoic acid. The SEM-EDX of [CTF(ZnO-TMP)] shows the grain and flower shapes are accumulated on the surface of hydrogels, and the clear presence of nano ZnO in the complex hydrogel. The TGA studies shows the loss of CH_2CH_2OH and carboxylate of 2-furoic acid of [CTF(ZnO- TMP)] hydrogel complex. Hence, the study conclude the good results in the synthesized biocompatible pH sensitive hydrogels which may have a remarkable applications in industrial and biological applications include metal ion removal, cationic dye removal, and controlled release of drugs to pH sensitive parts of human being.

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Does this article screened for similarity?

Yes

Conflict of interest

The Authors declares that there is no conflict of interest anywhere.

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