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RESEARCH ARTICLE

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Preparation of coumarin polymer grafted nanocellulose films to form high performance, photoresponsive barrier layers

Poornima Vijay[1] | Warren Batchelor[2] | Kei Saito[1,3]

[1]School of Chemistry, Monash University, Clayton, Victoria, Australia

[2]Chemical Engineering Department, Monash University, Melbourne, Victoria, Australia

[3]Graduate School of Advanced Integrated Studies in Human Survivability, Kyoto University, Kyoto, Japan

Correspondence
Kei Saito, Graduate School of Advanced Integrated Studies in Human Survivability, Kyoto University, Higashi-Ichijo-Kan, Yoshida-nakaadachicho 1, Sakyo-ku, Kyoto, 606-8306, Japan
Email: saito.kei.1y@kyoto-u.ac.jp

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Abstract

Hydrophobically modified cellulose is prepared in this research by conducting atom transfer radical polymerization (ATRP) of methacrylate substituted coumarin monomer on initiator grafted cellulose. The photocrosslinking of uniformly grafted coumarin on cellulose surface is applied to improve the water vapor barrier property of the film. The water vapor transmission rate (WVTR) of films prepared from modified cellulose with varying grafting density, grammage, and photocrosslinking time is studied. By increasing the amount of crosslinking within the grafted cellulose film, we succeeded in reducing WVTR. The WVTR is reduced from 160 to 20 g/m^2/day using a sheet of 60 g/m^2 after crosslinking. The effect of grafting density on WVTR is also analyzed to observe that the higher the grafting density, lower the WVTR of the sheet both before and after crosslinking. Furthermore, free ATRP polymerization (without cellulose) and polymerization using a sacrificial initiator of the monomer are conducted to estimate the dispersity of the polymer on cellulose. The monomer, free polymer and cellulose grafted polymers are analyzed for the composition, thermal, morphology, photoresponsive behavior, and polymerization quantification using NMR, FTIR, UV–Vis, TGA DSC, GPC, SEM, ICP-MS. It is concluded that the inter and intramolecular photo dimerization of coumarin molecules forms a hydrophobic crosslinked hyper network in the polymer sheet, which improves its barrier property.

KEYWORDS

atom transfer radical polymerization, coumarin, nanocellulose modification, photoresponsive polymer, water vapor transmission rate

1 | INTRODUCTION

Paper-based materials are extensively used in packaging materials because of their degradable, mechanical and renewable properties. The water vapor transmission rate (WVTR) of packing material is supposed to be low to extend the shelf life of moisture sensitive goods. However, traditional paper sheets possess poor water vapor barrier properties. The water vapor barrier properties of paper can be improved by increasing the hydrophobicity of paper and reducing its porosity.[1] Some synthetic polymeric hydrophobic materials such as vinyl alcohol copolymer and polyvinylidene chloride film are conventionally used to improve the water vapor barrier properties of the paper-based materials. These materials are nondegradable and challenging to recycle, which causes pollution to the environment.[2] Recently the incorporation of environmentally friendly materials on cellulose to improve its barrier properties has been investigated.[3] For example, the improvement of the barrier properties of cellulose sheets was achieved by taking cellulose nanofibres (CNF) as a base layer and coating it with cellulose nanocrystals (CNC), followed by montmorillonite clay and soy protein.[4] The idea was that the CNC is less sensitive to moisture than CNF due to its crystalline nature. A layer of montmorillonite clay between CNC and soy protein was used to balance cellulose and protein's hydrophilic and hydrophobic properties; they achieved a WVTR of 95 g/m^2/day.[4] To increase the hydrophobicity and decrease the pore size of the barrier film, CNF films have been coated with various materials such as starch, beeswax to close the surface pores and reduce the WVTR to 50 g/m^2/day.[5]

Many previous studies combined polylactic acid (PLA) and CNC. For example, the hydrophobically modified CNC was prepared by either (a) grafting hydrophobic monomers via free radical polymerization to improve the compatibility of CNC with PLA matrix in an organic solvent or (b) by using intermediate materials like surfactants to disperse CNC in hydrophobic PLA matrix.[6] A composite of 99% PLA in 1% CNC with 40 g/m^2 grammage reduced WVTR to 34 g/m^2/day.[7,8] It was explained that nanofillers act as blocking agents within the polymeric matrix to promote tortuosity and prevent water molecules' permeation.[9] Another report indicates the increase in barrier property of PLA/CNC composites is due to the increase in crystallinity with the addition of CNCs.[10] Other biodegradable polymers including poly(butylene adipate-co-terephthalate), poly (ε-caprolactone), poly(butylene succinate) and polyhydroxy butyrate have been used as matrices for CNC- based nanocomposite barriers.[11] The addition of CNCs increases the hydrophilicity of the polymer, which in turn increases the polymer degradation rate by causing hydrolysis of the chains in the environment.

One of the problems of CNC based nanocomposite is the poorer dispersion of CNC within the film due to its aggregation in the hydrophobic polymer matrix. Better dispersion of hydrophilic CNC with hydrophobic polymers can be achieved by establishing covalent bonding between two substrates. Covalent bonding between CNC and the matrix will improve the stability of CNC dispersion via steric stabilization provided by the grafted polymer chains and increases the compatibility of CNC with polymer matrix. One way to covalently bond the cellulose and the polymer is by ATRP (atom transfer radical polymerization). ATRP on cellulose with vinyl monomers, compared to other free radical polymerizations, is more efficient in growing uniformly distributed, monodisperse polymer chain on the surface of CNC with high graft density. In surface-initiated atom transfer radical polymerization (SI-ATRP), the initiator molecule is attached to the surface of CNC by utilizing surface —OH groups. Then, controlled polymerization of the vinyl monomer is conducted.[12] SI-ATRP of CNC with various vinyl and acrylate monomers like styrene, methyl methacrylate, *N*-isopropylacrylamide, butyl methacrylate has been used to control molecular weight and minimum molecular dispersity of the obtained polymers on CNC.[13–15]

Here in this research, we produced hydrophobically modified cellulose by grafting methacrylate substituted 7-hydroxy coumarin (umbelliferon) on cellulose using ATRP polymerization. Umbelliferon is a naturally occurring coumarin that can find in higher Ferula communis plants.[16] Coumarin undergoes a 2 + 2 reversible cycloaddition reaction to form a cyclobutene ring on the irradiation of the corresponding wavelength of UV light (365 and 250 nm, respectively).[17] The reversible photo-dimerization of polymers having coumarin has been widely studied with applications in refractive index tenable lenses, photoinduced bending polymers, self-healing materials, and optical data storage materials.[17–19] In this study, the photodimerization characteristic of polymer containing coumarin grafted on cellulose was studied for its barrier property.

Most of the previous reports describing the incorporation of coumarin on cellulose were done by attaching a single coumarin moiety to the cellulose molecule, not coumarin polymer chains.[20–22] A few recent articles deal with the polymerization of coumarin monomer on cellulose; however, their applications are not focused on controlling WTVR.[23,24] In this research, to the best of the author's knowledge, ATRP polymerization of monomer containing coumarin pendent group was conducted on cellulose for the first time.

Some of the studies have adapted controlled living radical polymerization, especially ATRP, for preparing a well-defined polymeric structure with coumarin, such as coumarin functionalized dendritic-star polymers.[25,26] In those papers, they stated the ATRP gave a well-defined structure (with controllable chain length) therefore coumarin-coumarin crosslinking was possible between adjacent arms of the dendrimer-star copolymers.[27] In this research, ATRP is used to control length of the polymer in similar way to enhance the cross-linking between coumarin molecules from adjacent chains. We hypothesis that the highly cross-linked network will lower WVTR. As far as the author's knowledge, this is for the first time the photocrosslinking of coumarin was studied for the application in barrier properties.

The materials used in polymer production are cellulose and coumarin; both are derived from natural sources and are biodegradable.[28] However, in order to establish covalent bond between coumarin and cellulose and conduct narrow molecular disperse polymerization using ATRP technique, methacrylate backbone is used.

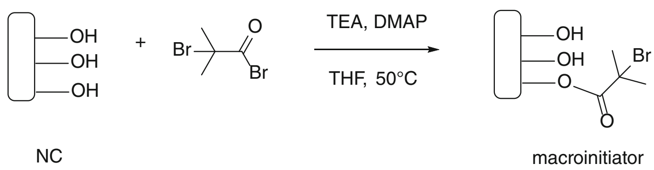
Nanocellulose (NC) produced in one pot treatment using sustainable reagents, Fe_2O_3/H_2O_2 was[29] taken as the precursor for grafting methacrylate substituted coumarin polymers. Owing to the higher surface area and the lower DP of the NC, the proficient grafting of the polymer was expected. Most of the previous reports regarding grafting cellulose,[30–33] have adapted the acid hydrolysis method of generating CNC from bleached microcrystalline cellulose. NC developed in one pot treatment has similar properties as acid hydrolyzed CNC, like its nano, uniform size, high crystallinity, and high surface area, with the added advantage of utilizing sustainable, mild reagents for its production.

The grafting from NC was established by attaching the initiator to the NC to form a macroinitiator and then conducting ATRP polymerization of the macroinitiator with monomers. The monomer, free polymer and polymer grafted on cellulose were analyzed using NMR, FTIR, UV–Vis, TGA, DSC, GPC, SEM, and ICP-MS instruments. At last, the photoresponsive properties of the polymers sheet and its effect on WVTR by varying grammages, grafting density and varying crosslinking times were studied.

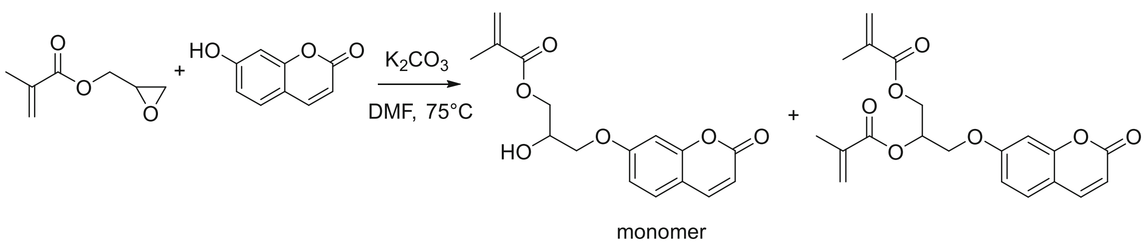
2 | RESULT AND DISCUSSION

2.1 | Reaction schemes

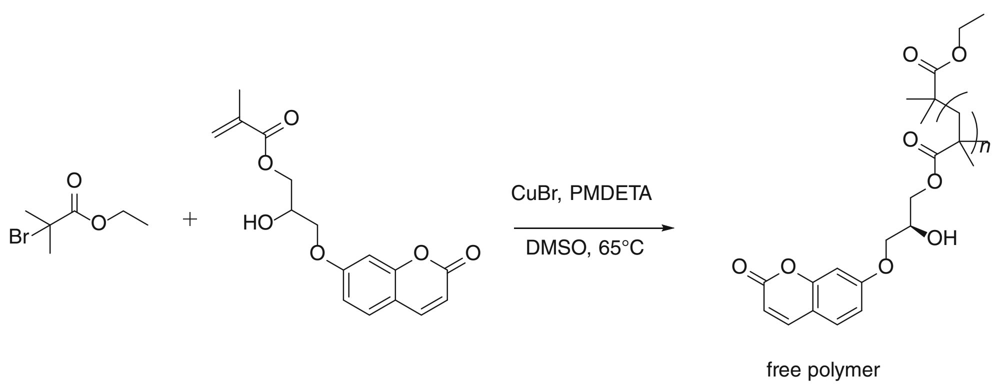
Scheme 1 shows the synthesis of coumarin containing two active products by reacting glycidyl methacrylate with 7-hydroxycoumarin. A single methacrylate substituted coumarin and a double methacrylate substituted coumarin was obtained. Single methacrylate substituted coumarin was carefully separated from the other using column chromatography to avoid the formation of the crosslinked structure during the polymerization. This functional monomer was taken for further polymerization reactions. The monomer was polymerized using the initiator, ethyl α-bromoisobutyrate (Ebib), through the ATRP polymerization technique as shown in Scheme 2 to produce the free polymer. The purpose of the synthesis of the free polymer was to study its properties and to have a better understanding of the polymerization of the monomer, such as its molecular weight and molecular dispersity. Scheme 3 shows the synthesis of the macroinitiator. Macroinitiator was synthesized by reacting NC with Bromo isobutyryl bromide (Bbib). The macroinitiator produced in Scheme 3 was utilized to polymerize monomer through ATRP polymerization along with the sacrificial initiator in Scheme 4 to produce polymer grafted NC (NC-polymer) and polymer from the sacrificial initiator in solution. All the products from Schemes 1 to 4,



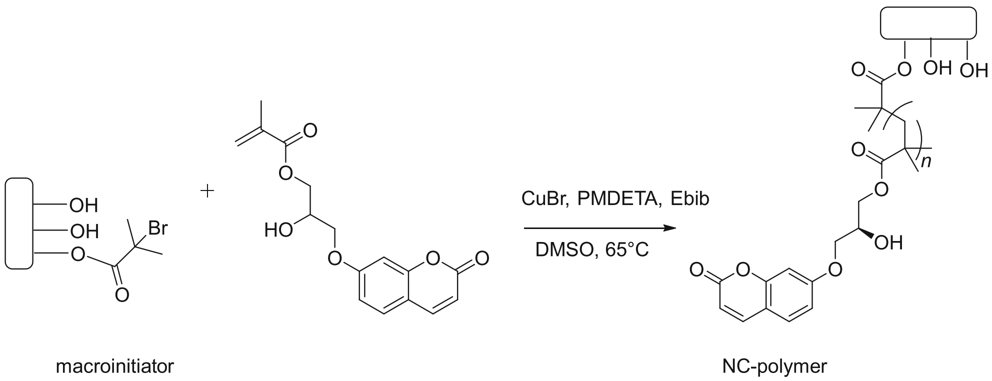
SCHEME 3 Macroinitiator synthesis.



SCHEME 1 Active monomer synthesis



SCHEME 2 Free polymer synthesis.



SCHEME 4 Polymer grafted on NC (NC-polymer) synthesis

that is, monomer, free polymer, macroinitiator, polymer from sacrificial initiator and NC-polymer, were characterized in the following section.

2.2 | Characteristic analysis

2.2.1 | FTIR analysis

The FTIR spectra of NC and macroinitiator are given in Figure 1A. There is a carbonyl peak at 1735 cm^{-1} in macroinitiator spectra. This result supports that the Bbib group has successfully attached to the NC in the macroinitiator.

In FTIR spectra (b), the FTIR of monomer, free polymer and NC-polymer are given. Peaks at 3073 and 1644 cm^{-1} are only visible in monomer spectra, corresponding to the =C—H stretch and C=C in alkenes. Also, a peak at 806 cm^{-1} can only be seen in the monomer peak, corresponding to the =C—H bending. In both free polymer and NC-polymer, these three peaks mentioned above completely disappear, confirming the vinyl group's utilization in polymerization.

A peak at 1700 cm^{-1} is present in all three spectra (monomer, free polymer and NC-polymer), corresponding to the methacrylate group's carbonyl peak. A peak at 1600 cm^{-1} corresponds to the aromatic C=C stretching of the coumarin molecule, present in all three spectra. These results strongly emphasize monomer, free polymer, and NC-polymer functional groups.

2.2.2 | NMR analysis

^{1}H NMR of monomer and free polymer are given in Figure 2A,B. Figure 2A shows a pure monomer with all the peaks corresponding to coumarin condensation with a single molecule of glycidyl methacrylate. However, all the peaks in Figure 2A have been replaced in Figure 2B by broadened peaks with a chemical shift corresponding to the polymer protons, with the complete disappearance of vinyl protons (6,6′) of monomer at around 5.5 ppm. This result confirms the formation of the free polymer.

2.2.3 | GPC of free polymer and the polymer from the sacrificial initiator

As shown in Table 1 and Figure S1, the molecular dispersity (ÐM) of free polymer gave a value of 1.23. The number average molecular weight (M_n) was 15,400.

The ÐM being 1.23 suggests a narrow molecular weight distribution. Further, as shown in Table 2 and Figure S2, the ÐM of the polymer in the solution produced by the sacrificial initiator was 1.63. The idea of using a sacrificial initiator in ATRP is that the polymer growth from the sacrificial initiator can be correlated with that of the macroinitiator.

The low molecular dispersity value of the polymer on the sacrificial initiator indicates the controlled chain length and well-defined structure of the coumarin molecules on the cellulose nanoparticles.

ATRP polymerization is highly thought of in this research to obtain uniform polymer chain length on cellulose surfaces. The uniform chain length of the polymer containing the coumarin pendent group will be highly susceptible to crosslinking with adjacent (intermolecular) coumarin molecules when they are subjected to UV crosslinking, similar to what was explained in literature.[25–27]

2.2.4 | Quantification of Br group in macroinitiator and cu in NC-polymer

ICP-MS analysis of macroinitiators (A), (B) and (C) show 1.4 ± 0.1, 4 ± 0.2, and 7.7 ± 0.1 wt.% of Br group in macroinitiators (Standard calibration curve is shown in Figure S4).

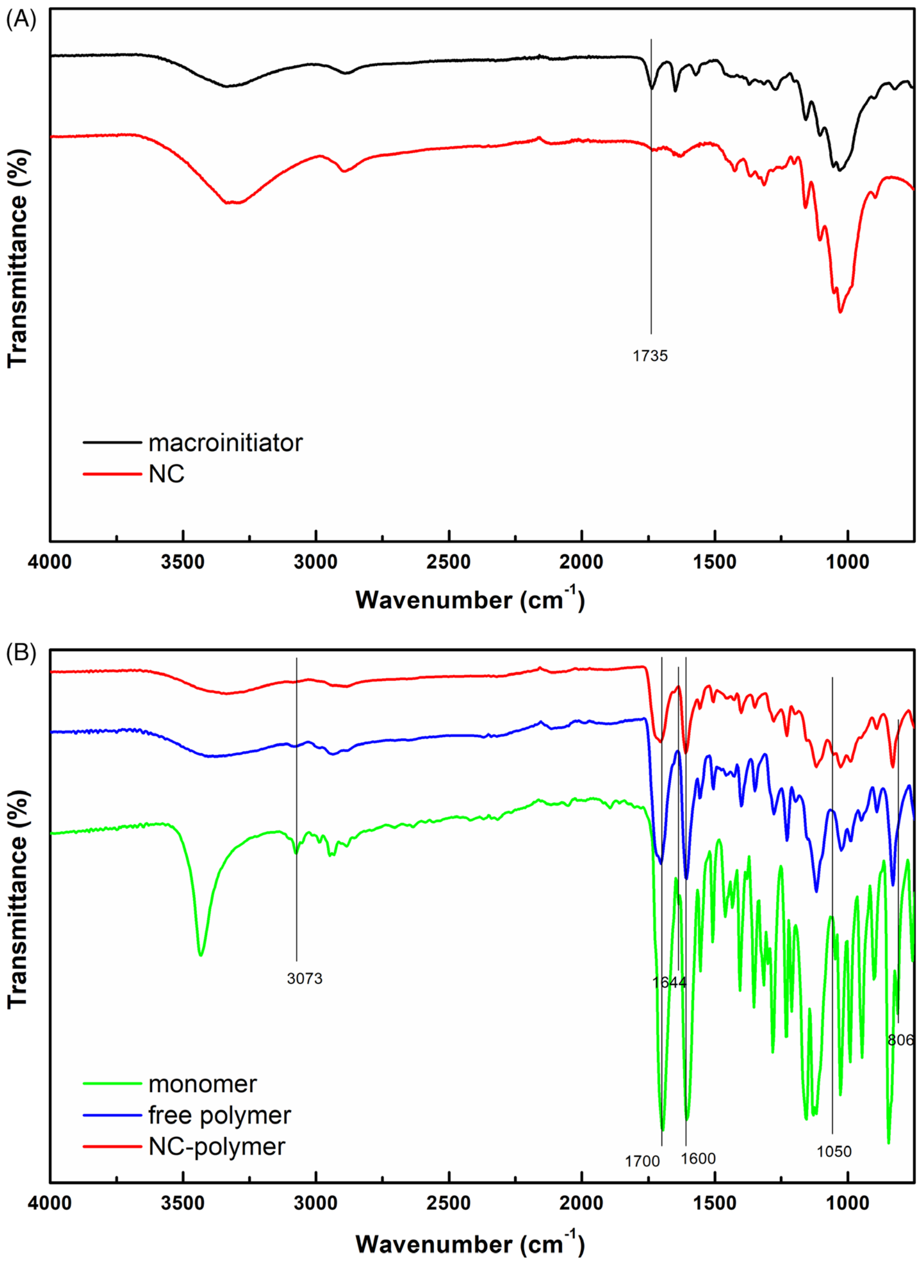


FIGURE 1 FTIR of (A) NC and macroinitiator, (B) monomer, free polymer, and NC-polymer

The amount of residual copper present in NC-polymer was 0.1 ± 0.02 wt.%.

2.2.5 | TGA, DSC analysis

TGA of NC, free polymer and NC-polymer are given in Figure 3A–C, respectively. The weight loss pattern of NC-polymer is having a first significant weight loss at 265°C, which is the same as that of NC. Hence, around 35% weight loss at 260°C can be predicted to correspond to the NC present in the NC-polymer. The second significant weight loss, about 45% at 335°C, is different from that of NC and free polymer. This new weight loss pattern at 335°C is due to the polymer grafted on NC. This result proves the covalent bonding between cellulose and coumarin polymer. Also, the NC-polymer shows improved thermal behavior of grafted polymer on NC.

DSC curves of free polymer, NC-polymer and NC are given in Figure S3. T_g of the free polymer was 85.9°C, T_g of the NC was 158°C, whereas T_g of the NC-polymer was 103°C. The rise in T_g of NC-polymer compared to free polymer could be due to the rigid nature of NC covalently attached to the polymer.

2.2.6 | Solid-state ^{13}C NMR

The cellulose being an insoluble material in most solvents, solid-state ^{13}C NMR is a valuable tool for analyzing

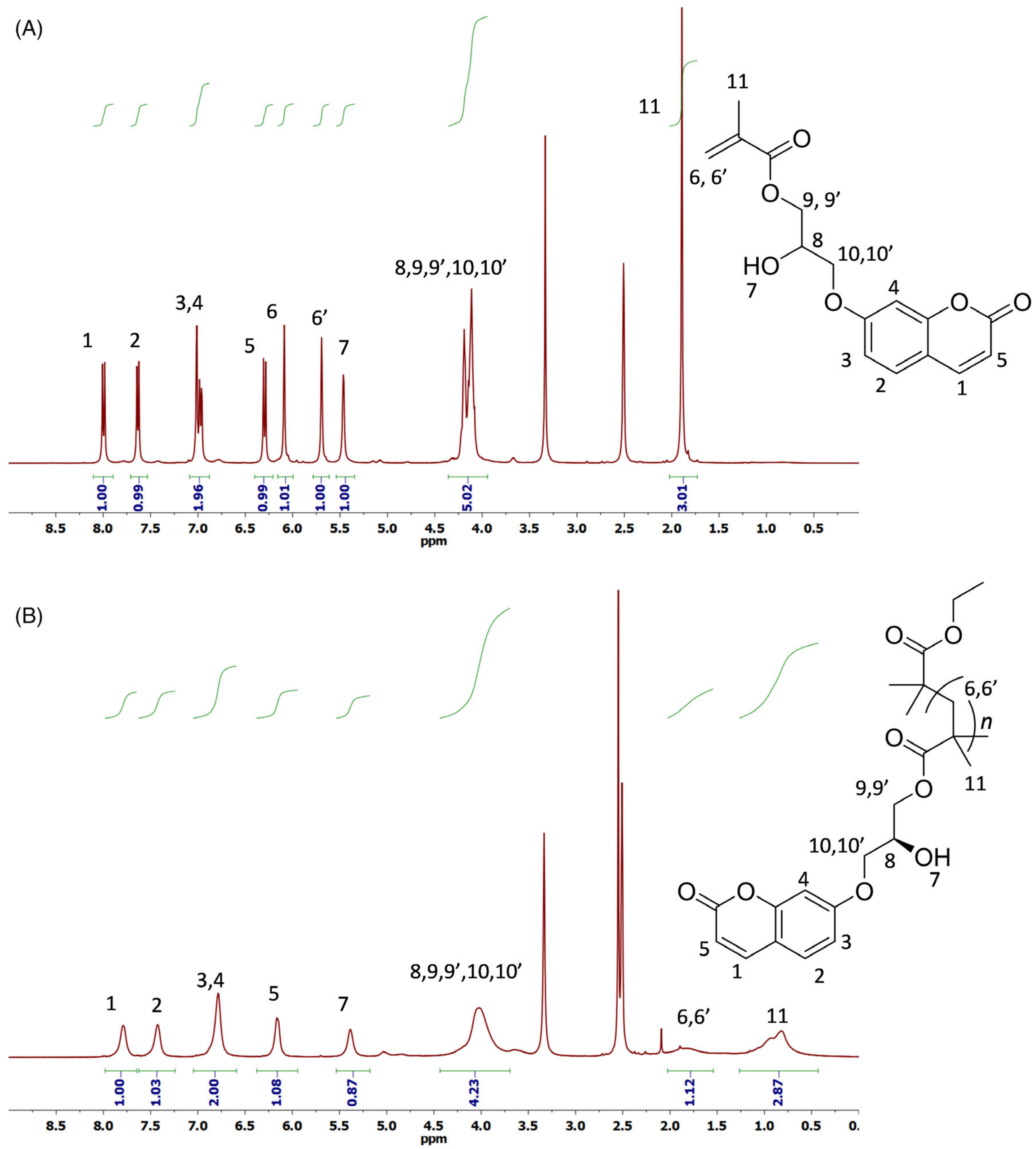


FIGURE 2 ^{1}H NMR of (A) monomer and (B) free polymer

TABLE 1 GPC result of free polymer

Peak	Material	Retention time (min)	Area (%)	M_n	M_w	ĐM
1	Free polymer	13.6	93.5	15,400	19,400	1.23
2	Monomer	16.7	6.4	170	190	1.09

TABLE 2 GPC result of polymer in solution using a sacrificial initiator

Peak	Material	Retention time (min)	Area (%)	M_n	M_w	ĐM
1	SIPolymer-1	13.8	97.2	11,600	18,900	1.63
2	SIPolymer-2	10.05	2.8	494,100	790,000	1.59

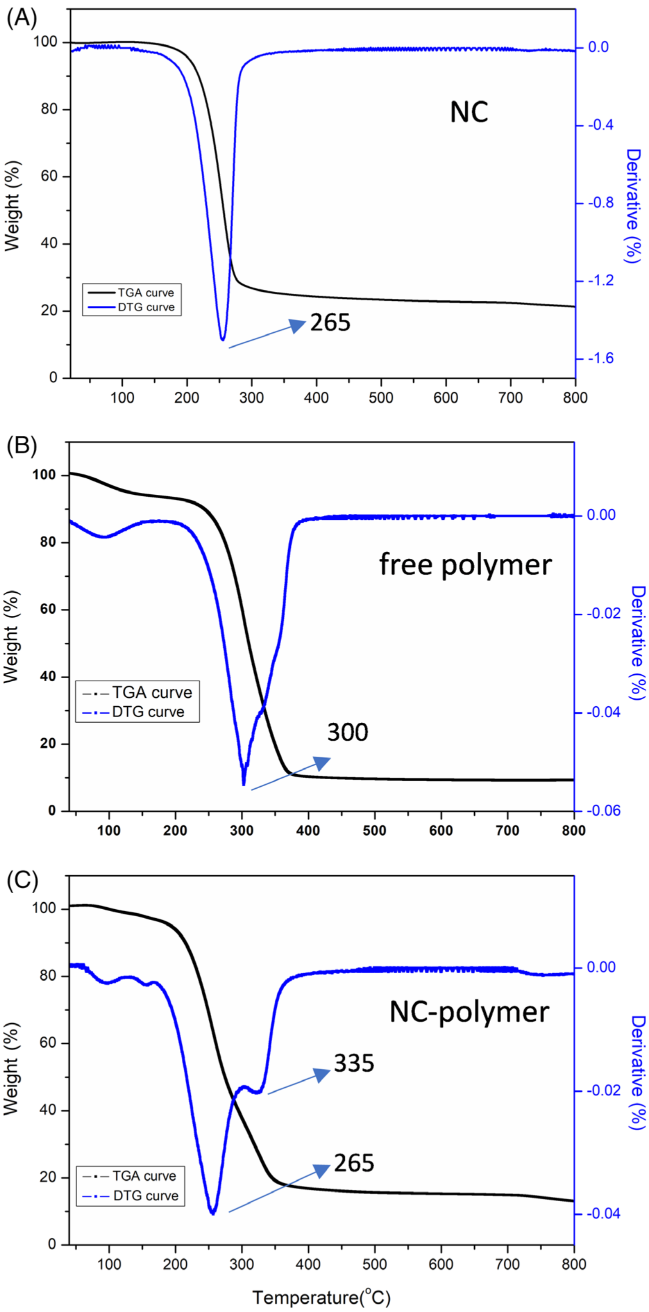


FIGURE 3 TGA analysis of (A) NC, (B) free polymer, (C) NC-polymer

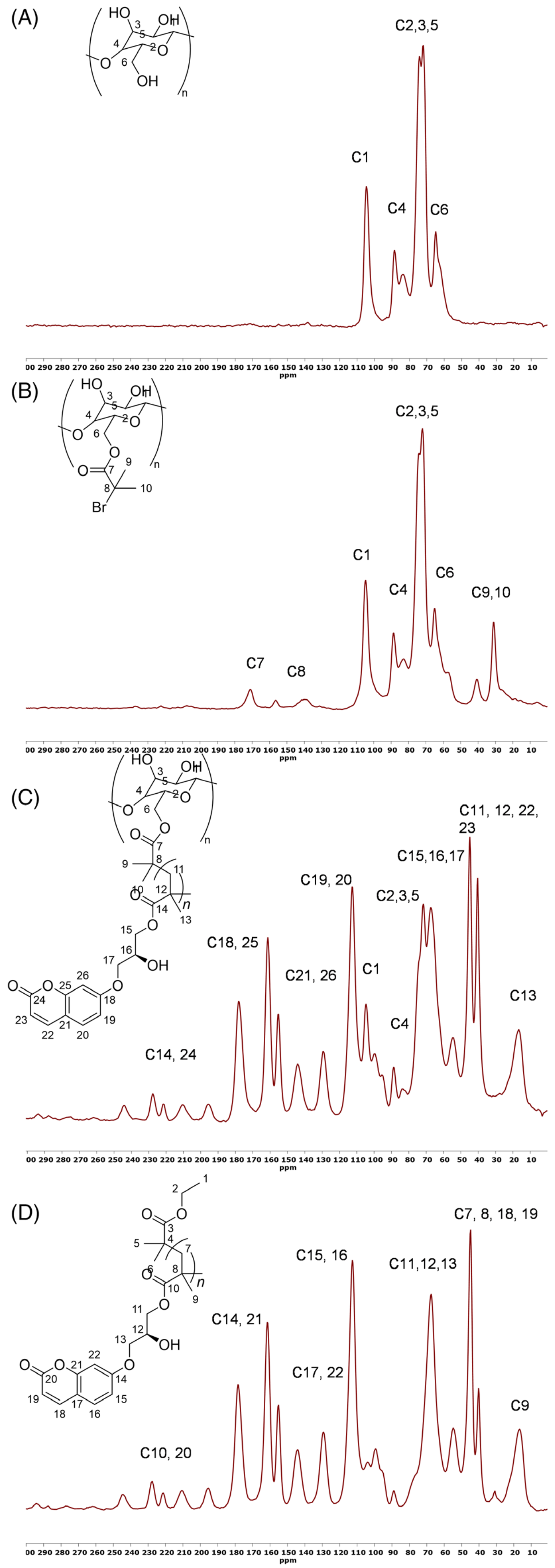


FIGURE 4 Solid-state ^{13}C NMR of (A) NC, (B) macroinitiator, (C) NC-polymer, (D) free polymer

the structural properties of polymers grafted on cellulose. The solid-state ^{13}C NMR of NC, macroinitiator, free polymer and NC-polymer are given in Figure 4. The solid-state ^{13}C NMR of the macroinitiator (Figure 4B) shows all the peaks corresponding to cellulose and the peaks corresponding to the Bbib group of macroinitiator, that is, the methyl carbon at 30 ppm, C—Br at 40 ppm and ester group carbon at 170 ppm. This result confirms the attaching of the Bbib group on NC. Further, NC-polymer (Figure 4C) shows all the peaks corresponding to NC (Figure 4A) with that of free polymer (Figure 4D). The ^{13}C peaks belonging to aromatic coumarin moiety range from 110–150 ppm, and the ester group is from 160–240 ppm. All these peaks strongly emphasize the grafting of polymer on NC.

2.3 | Photoresponsive properties of the polymer

Photo responsiveness of NC-polymer membrane on quartz slide (NC-polymer [quartz slide]) was analyzed. The membrane was irradiated with 365 nm wavelength for varying times from 0–16 h using a photo crosslinker. A progressive increase in crosslinking of the coumarin group in the membrane was analyzed using a UV–Vis spectrometer, as shown in Figure 5. The crosslinking extent of the NC-polymer membrane proceeded to 50% in 8 h.

To confirm the crosslinking in the sheet, NC-polymer-S; The FTIR of the sheet before and after crosslinking was analyzed. The FTIR of NC-polymer-S and NC-polymer-S-CL are shown in Figure 6.

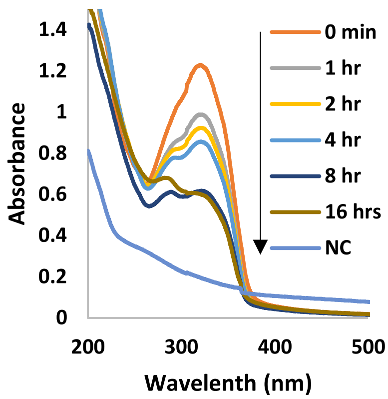


FIGURE 5 Crosslinking of the membrane NC-polymer (quartz slide) using UV-crosslinker of 365 nm at a different time interval

As shown in Figure 6, there are many changes in peak position in the spectra of the crosslinked sheet, NC-polymer-S-CL, compared to that of the sheet before crosslinking, NC-polymer-S. The main differences are that a peak at 1648 cm^{-1} in NC-polymer-S corresponds to the C═C stretching of the coumarin alkene group, which has diminished in the case of NC-polymer-S-CL because of the dimerization of coumarins. A peak at 1275 cm^{-1} in NC-polymer-S, which corresponds to the C—O stretching of the aromatic ester group, has changed its position in NC-polymer-S-CL due to the change in the environment because of crosslinking. A shift in peak position at 830 cm^{-1} is due to the C═C bending in the coumarin alkene group before and after crosslinking. All these observations confirm the dimerization of coumarin in the NC-polymer-S-CL sheet.

2.4 | Effect of grammage and crosslinking time on water vapor transmittance rate of the polymer

Filter paper (base sheet), NC-polymer-S (made by NC-polymer) of different grammage of 40, 60, and 80 g/m^2 were tested for their WVTR before and after UV irradiation for varying time intervals of 4, 8, 10, and 12 h as shown in Figure 7.

WVTR of base paper was 550 g/m^2/day. Sheets made up of NC-polymer on base paper with a grammage of 40 g/m^2 gave WVTR of 220 g/m^2/day; a drastic decrease of 60% value in WVTR compared to base paper was observed. Sheets with a higher grammage of 60 and 80 g/m^2 gave a reduction in WVTR of 70% and 75% (i.e., 163 and 140 g/m^2/d), respectively. This decrease in WVTR on forming a layer of NC-polymer on filter paper was due to the higher hydrophobic nature of the NC-polymer. As

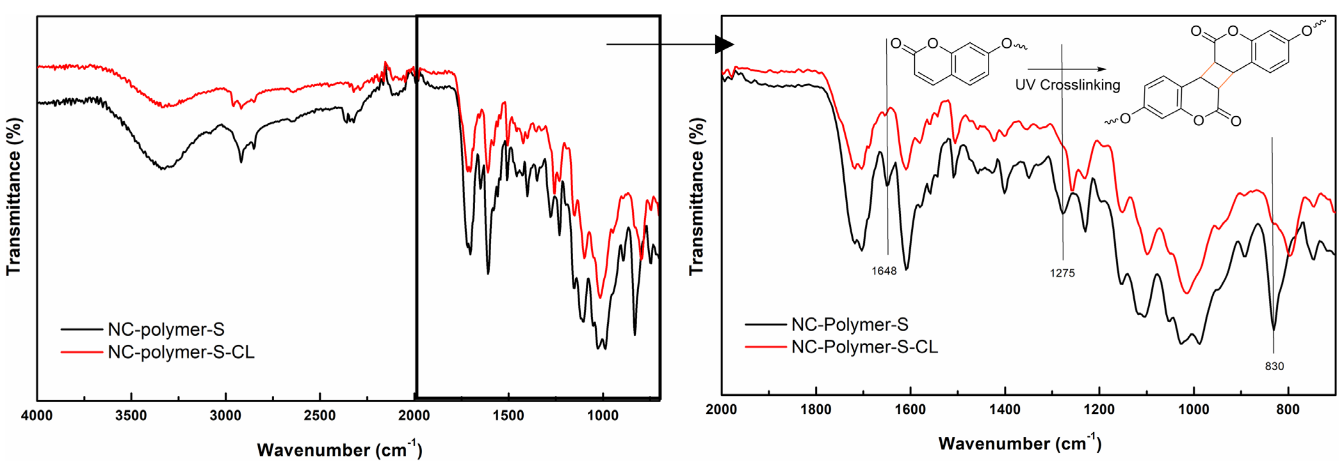


FIGURE 6 FTIR of NC-polymer-S and NC-polymer-S-CL

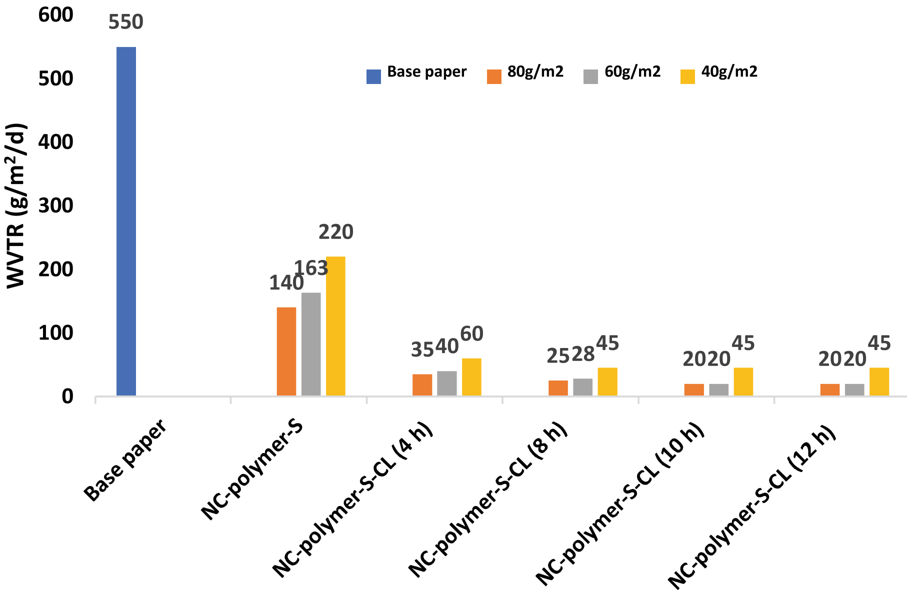


FIGURE 7 WVTR measurements of base paper and NC-polymer-S and NC-polymer-S-CL sheets at a varying crosslinking time interval and varying grammage

the thickness (grammage) of the NC-polymer-S increased, the WVTR decreased; the reason is thought to be the increase in the relative path traveled by the water vapors also due to the torturous path created on the base paper by the NC-polymer sheet, similar to what was explained in the literature.[9]

The coumarin molecules in NC-polymer-S were made to crosslink by keeping the sheet in a UV crosslinker for 4, 8, 10, and 12 h. The sheet NC-polymer-S-CL (4 h) with 40 g/m^2 grammage showed a WVTR of 60 g/m^2/day, that is, 73% decrease compared to noncrosslinked NC-polymer-S, which showed a WVTR of 220 g/m^2/day. Whereas, after 8 h of crosslinking, the WVTR was decreased to 80% as compared to noncrosslinked NC-Polymer -S (220 g/m^2/day), with the value of WVTR being 45 g/m^2/day. Further increase in crosslinking time did not affect the WVTR of the sheet.

Four hours of crosslinking of NC-Polymer-S with 60 g/m^2 showed the WVTR, 40 g/m^2/day, 75% lower than the noncrosslinked sheet (163 g/m^2/day). After 8 h of crosslinking, WVTR has reduced to 28 g/m^2/day, that is, an 83% decrease in WVTR value than that of the non-crosslinked sheet (163 g/m^2/day) was observed. After 10 h of crosslinking, an 88% decrease in WVTR as compared to the non-crosslinked sheet (163 g/m^2/day) was witnessed with a WVTR value of 20 g/m^2/day. Further increase in crosslinking time did not alter the WVTR.

With NC-polymer-S with grammage, 80 g/m^2, after 4 h of irradiation, a 75% decrease in WVTR (35 g/m^2/day) compared to the noncrosslinked sheet (140 g/m^2/day) was observed. After 8 h of crosslinking further 8% decrease in WVTR (25 g/m^2/day) was observed. When 10 h of crosslinking was conducted, a constant WVTR of 20 g/m^2/day was reached.

All sheets with varying grammage show a decrease in WVTR on the increase in UV crosslinking time till 10 h. After that, a further rise in crosslinking time did not affect the WVTR. Hence, crosslinking is assumed to reach its maximum on irradiation for 8–10 h. Therefore, there was no improvement in WVTR at 12 h of irradiation.

Sheet with 40 g/m^2 showed the lowest of 45 g/m^2/day of WVTR when irradiated for 8 h. Sheet with 60 g/m^2 gave a minimum WVTR value, 20 g/m^2/day. The lower WVTR in the case of 60 g/m^2 was due to the higher thickness and higher crosslinking of molecules. Whereas, when the 80 g/m^2 sheet was used, the minimum WVTR reached was 20 g/m^2/day which was the same as that obtained from the 60 g/m^2 sheet. This can be explained as the crosslinking of coumarin takes place as far as the UV light reaches the coumarin molecules on the NC-polymer-S surface. However, beyond the reachability of UV light, the coumarin in NC-polymer will not get crosslinked and hence, in the case of a crosslinked sheet of 60 and 80 g/m^2, show the same WVTR. Even though there was a difference in the WVTR of the two sheets before crosslinking (due to the longer torturous path of water vapor), the WVTR value became the same after crosslinking. Thus, the value of 60 g/m^2 grammage of NC-polymer-S with 10 h of irradiation is considered the best condition to obtain the minimum WVTR results (20 g/m^2/day).

2.5 | Effect of grafting density on WVTR of NC-polymer-S

NC-polymer with different grafting densities were synthesized to analyze the effect of grafting density to

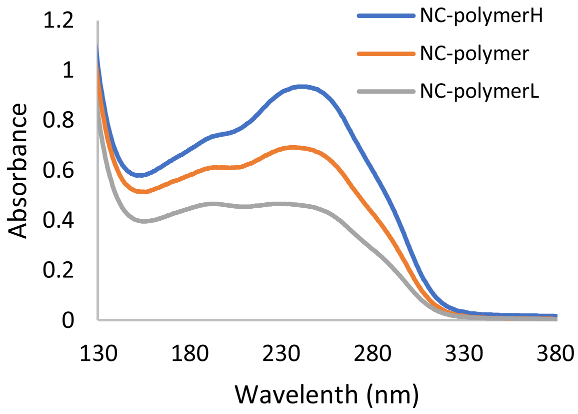


FIGURE 8 UV–vis spectra of 0.002 wt.% NC-polymerL, NC-polymer, NC-polymerH in DMSO

WVTR. The grafting densities were evaluated by finding the amount of monomers in the polymer using UV–vis spectra. The UV–vis spectra of NC-polymers in the solution state are given in Figure 8.

The amount of monomer in NC-polymer, NC-polymerL, and NC-polymerH were analyzed to be 66, 43, and 89 wt.%, respectively. A calibration curve using known concentrations of monomer for the analysis is given in Figure S8.

In Section 2.4, it is experimentally analyzed that sheet made from NC-polymer with 60 g/m^2 has a minimum WVTR of 20 g/m^2/day. Therefore, in this section, to find the effect of grafting density on the WVTR, the grammage of the sheet was fixed to 60 g/m^{2,} and the UV irradiation time was carried out for 10 h for the sheets prepared from other polymers.

The WVTR of the 60 g/m^2 sheets formed using NC-polymer, NC-polymerL. and NC-polymerH are given in Table 3.

From Figure 7, it is known that the base paper alone has the WVTR of 550 g/m^2/day. The sheet prepared from NC-polymerL with a grafting density of 43 wt.% monomer in it in it gave a WVTR value of 300 g/m^2/day before crosslinking. That is a decrease in 46% of WVTR is observed as compared to that of the base paper. On the other hand, the sheet prepared from NC-polymer and NC-polymerH with a grafting density of 66% and 89% monomer in them; showed a 70% and 75% decrease in WVTR (i.e., 163 and 140 g/m^2/day, respectively) before crosslinking as compared to the base paper. Because of the lower grafting density of the NC-polymerL, the WVTR of the sheet is higher as compared to NC-polymer and NC-polymerH. This could be explained by the hydrophobic effect of the sheet.

On UV irradiation of the sheets for 10 h, the sheet prepared from NC-polymerL showed a WVTR of 160 g/m^2/day,

TABLE 3 WVTR of NC-polymerL, NC-polymer, and NC-polymerH before and after crosslinking

NC-polymer	Monomer wt.% in NC-polymer.	WVTR (without crosslinking)	WVTR (after 10-h irradiation)
NC-polymerL	43%	300	160
NC-polymer	66%	163	20
NC-polymerH	89%	140	13

that is, a total of 70% decrease in WVTR compared to the base paper. The sheet prepared from NC-polymer gave WVTR of 20 g/m^2/day, that is, 96% decrease in WVTR compared to the base paper. The sheet prepared from NC-polymerH showed 13 g/m^2/day, which is a 98% decrease in WVTR as compared to the base paper. Hence the crosslinking in the case of highly grafted polymers like NC-polymer and NC-polymerH have a drastic effect on WVTR. This can be explained as the more the amount of coumarin molecules in the sheet, the more the crosslinking and network structure formation prevent the water vapor from passing through the sheets. Hence, the grafting density of the polymer sheet is inversely proportional to WVTR.

2.6 | Morphological analysis (SEM analysis)

NC-polymer taken for SEM analysis is NC-polymer. SEM images of NC, NC-polymer (on a silicon wafer), crosslinked NC-polymer (on a silicon wafer), NC-polymer-S and NC-polymer-S-CL are given in Figure 9. Images (A) and (B) show NC, where clusters of nanoparticles can be seen. NC taken for this research has a pure cellulose molecular structure,[29] without any substitution groups to attain electrostatic repulsion (as in TEMPO-oxidized CNC or acid hydrolyzed CNC). Hence, NC tends to form clusters. Whereas in Figure 9C, which represents the NC-polymer (on a silicon wafer), the particles have a uniform distribution. The polymer helps the nanoparticles disperse evenly on the surface of the slides. Figure 9D is crosslinked NC-polymer (on a silicon wafer) (NC-polymer-CL), where the particles form the network between each other. Crosslinking coumarin molecules in the polymer helps create a hyper network between the particles, clearly visible in Figure 9D. Thus, every particle is well connected to the adjacent particles, forming a filled network structure.

Figure 9E,F are NC-polymer-S sheets taken for WVTR analysis. The dense particles distributed on the

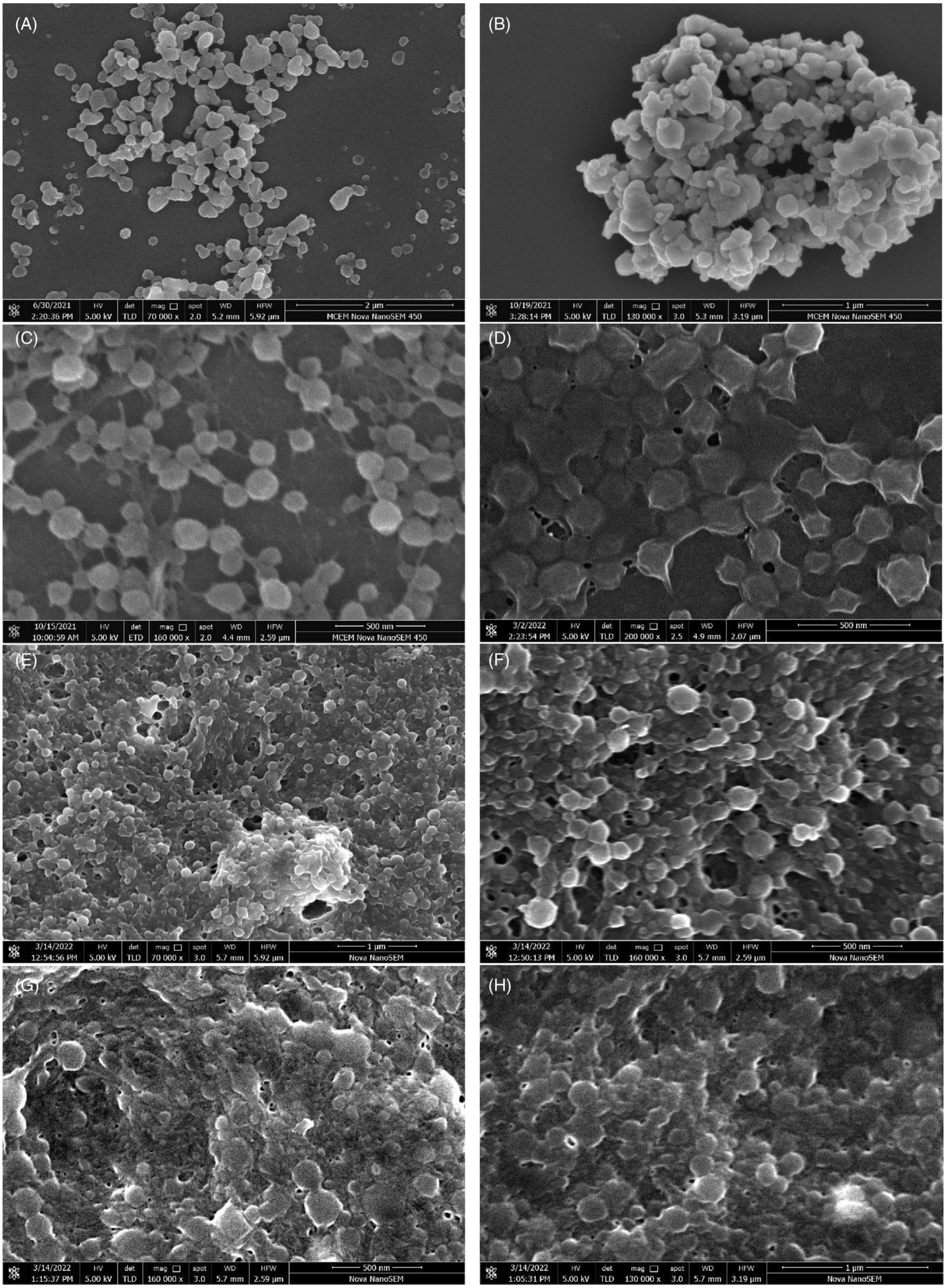


FIGURE 9 SEM analysis of (A), (B) are of NC; (C) is NC-polymer (silicon wafer), (D) NC-polymer-CL (silicon wafer), (E), (F) are the of NC-polymer-S and (G) and (H) are NC-polymer-S-CL (10 h)

surface show pores of up to around 500 nm in diameter. Figure 9G,H are of NC-polymer-S-CL, where the sheet was irradiated with a UV wavelength of 365 nm for 10 h. In Figure 9G,H, the pores between the particles have been filled or reduced to less than 50 nm diameter.

2.7 | Water contact angle measurement

The water contact angle measurement in Figure S5 shows the contact angle of NC-polymer-S and NC-polymer-S-CL (10 h) sheets. The contact angle of NC-polymer-S was 66.8°. During the measurement, the water droplet sinks into the sheet rapidly. Whereas the NC-polymer-S -CL sheet had a contact angle of 101.5°, the water droplet stayed in place without sinking for a few seconds. During the crosslinking of the coumarin molecule in the NC-polymer-CL sheet, the hydrophobic crosslinking network was formed under the influence of UV light. The crosslinking of the coumarin molecules on the surface forms a crosslinked network to form a tight barrier film, which is believed to help the droplet stay in place for a longer time.

Overall, two factors play an essential role in decreasing the WVTR of sheets. The first one is the hydrophobicity of NC-polymer, which is not favorable for water vapor to travel through the sheet. The second is the crosslinking of the coumarin molecules in the sheet. Even though one molecule of coumarin crosslinks with only one molecule of adjacent coumarin, each polymer chain contains multiple coumarin molecules, which can crosslink with nearby molecules, as shown in the schematic representation in Figure S6. The ATRP polymerization gave the advantage by uniformly distributing coumarin on the surface. Hence, more coumarin can crosslink to form a network in the NC-polymer sheet. Thus, improved WVTR was observed.

3 | CONCLUSION

A monomer with a single substituted glycidyl methacrylate of coumarin was synthesized and purified. The monomer was analyzed using IR and proton NMR. The pure monomer was taken for ATRP polymerization to prepare free polymer. Free polymer yield and proton NMR confirmed the high conversion of monomer to free polymer and its purity. GPC of the free polymer showed the molecular dispersity value of 1.2, indicating the narrow molecular weight distribution. The same reaction condition was applied on initiator grafted cellulose to prepare polymer grafted on cellulose (NC-polymer). The molecular dispersity of polymer in solution using a sacrificial initiator was 1.63. TGA of grafted cellulose showed a new weight loss pattern corresponding to the (NC-polymer). ^{13}C NMR of NC-polymer showed peaks of cellulose with that of free polymer. All analytical results strongly support the grafting of polymer from NC with narrow dispersity.

NC-polymer was inspected for its photoresponsive behavior. It took 8 h to crosslink coumarin in a thin membrane of NC-polymer to its saturation. Fifty percent crosslinking was observed. WVTR of sheet formed using NC-polymer on filter paper (NC-polymer-S) at 40, 60, and 80 g/m^2 grammage were studied by varying crosslinking time. As crosslinking time increased, the WVTR decreased until it reached a constant value after 10 h of crosslinking of the sheet. A minimum WVTR value, 20 g/m^2/day, was obtained using 60 g/m^2 grammage of NC-polymer-S on crosslinking for 10 h.

To understand the effect of grafting density of polymer on WVTR, sheets produced by polymers with three different grafting densities were analyzed. It was observed that the sheet with higher grafting density gave a minimum WVTR both before and after crosslinking.

SEM images and contact angle measurements indicated the crosslinked network structure of NC-polymer-S-CL.

ATRP polymerization promoted the uniform molecular weight distribution of the polymer chains (as per the GPC results). The uniform distribution of coumarin groups on the uniformed polymer chains tends to crosslink to a greater extent (as described in the introduction with examples[25–27]), resulting in a continuous network, which prevents water vapor from passing through the sheet, thereby decreasing the WVTR of the sheets (as per the data in Section 2.4). Improving WVTR using photocrosslinking of coumarin polymer grafted on NC is a new concept proved in this research. The future scope of NC-polymer will be by studying its property in solution form and the possible application as a cosmetic material with its UV absorbance characteristics.

4 | EXPERIMENTAL SECTION

4.1 | Materials

Pinewood sawdust was supplied by a local sawmill based in Melbourne, Australia. Hydrogen peroxide (H_2O_2) solution (30 wt.% in water), Fe_2O_3 (≤5 μm), 7-hydroxycoumarin, DMF, anhydrous K_2CO_3, glycidyl methacrylate, HCl, DMSO, copper bromide, *N, N, N′,N′′,N′′*-pentamethyldiethylenetriamine(PMDETA), Ethyl α-bromoisobutyrate (Ebib), acetone, chloroform, THF, Triethylamine, 4-dimethyl aminopyridine, Bromo isobutyryl bromide (Bbib), silica gel and nitric acid were purchased from Sigma Aldrich. Advantec filter paper, grade no 1 was purchased from Labtek Pty Ltd.

4.2 | Synthesis

4.2.1 | Nanocellulose synthesis

NC was synthesized by modifying our previous work.[24] Briefly, pinewood saw dust (5 g, oven-dried) was taken in a round-bottomed (RB) flask with 30% H_2O_2 (125 ml). The mixture was stirred and sonicated for 10 min. Next, 5 wt.% of iron oxide (Fe_2O_3) was added to the RB flask and sonicated for 10 min. The reaction mixture was heated to 90°C with stirring. After 2 h, another portion of H_2O_2 (125 ml) was added to the reaction mixture. The reaction continued for four more hours. Next, the reaction mixture was cooled and filtered. The solid product was taken in a beaker with DI water (100 ml), stirred for 10 min, and filtered. The product (NC) was dried in a freeze drier for 2 days and taken for further reactions.

4.2.2 | Active monomer synthesis

7-hydroxycoumarin (0.037 moles) was taken in an RB flask with DMF (30 ml). Anhydrous K_2CO_3 (0.037 moles) was added to the RB flask. The reaction mixture was stirred at 70°C. Glycidyl methacrylate (0.0185 moles) was taken with DMF (40 ml) in a dropping funnel. Glycidyl methacrylate was added to the reaction mixture dropwise for 2 h. The reaction mixture was continued stirring for 24 h at 70°C. The reaction mixture was cooled and filtered. The solid was washed with DMF (10 ml). The filtrate was taken in a dropping funnel and added slowly to the conical flask containing 5% HCl. The product was extracted from an acidic aqueous mixture using chloroform. The organic layer was washed with 1% K_2CO_3 in water. The organic layer was dried over magnesium sulfate and concentrated using rotavap.

The crude product was purified using column purification using silica gel as the stationary phase and n-hexane, ethyl acetate as the mobile phase. A single methacrylate substituted coumarin monomer was separated and analyzed using NMR and FTIR. ^{1}H NMR (400 MHz, [D$_6$] DMSO, 25°C, TMS): $\delta = 1.85$ (s, 3H), $\delta = 4.1$–4.25 (m, 5H), $\delta = 5.52$ (s, 1H), $\delta = 5.78$ (s, 1H), $\delta = 6.11$ (s, 1H), $\delta = 6.34$ (d, 1H), $\delta = 7.03$ (m, 2H), $\delta = 7.61$ (s, 1H), $\delta = 8.03$ ppm (d, 1H) [Figure 2A]; ATR-FTIR: 3432, 3073, 1700, 1600, 1644, 1554, 1506, 1462, 1429, 1402, 1354, 1314, 1284, 1233, 1210, 1159, 1122, 1027, 987, 946, 899, 842, 806, 754 cm^{-1} (Figure 1B, monomer). The monomer was taken for polymerization.

4.2.3 | Free polymer synthesis

Monomer (0.5 g, 1.65 mmol) was taken in DMSO (1 ml) and stirred until all dissolved. Conducted freeze-vacuum-thaw cycles three times to remove all the air trapped in the mixture. Copper bromide (0.033 mmol) and PMDETA (0.033 mmol) to the degassed mixture were added and stirred under argon gas for 30 min. The reaction mixture was heated to 65°C. Ebib (0.033 mmol) was added to the reaction mixture. The reaction mixture was stirred at 65°C for 24 h. The reaction mixture was slowly dropped into acetone (50 ml). The precipitated polymer was centrifuged and separated and dried in an oven. 0.3 g (60 wt.% monomer conversion) of the free polymer was obtained. The polymer was analyzed using GPC, FTIR, NMR, TGA, and DSC. ^{1}H NMR (400 MHz, [D$_6$] DMSO, 25°C, TMS): $\delta = 0.65$–1.18 (b, 3H), 1.6–2.05 (b, 1H), 3.75–4.25 (b, 5H), 5.25–5.49 (b,1H), 6.14–6.25 (b, 1H), 6.65–6.82 (b, 2H), 7.32–7.71 (b, 1H), 7.75–7.89 ppm(b,1H) (Figure 2B); ATR-FTIR: 3395, 3081, 1709, 1604, 1550, 1506, 1398, 1348, 1277, 1226, 1193, 1115, 1024, 990, 950, 889, 828 cm^{-1} (Figure 1B, free polymer); GPC: $M_n = 15{,}400$ $M_w/M_n = 1.23$ (Figure S1, Table 1).

4.2.4 | Macroinitiator synthesis

Initiator modified cellulose was synthesized according to the previously performed method with few changes.[13] Macroinitiators with three varying Bbib groups are synthesized by adding different amounts of Bbib and keeping the other reagent amount constant. Three reaction setups were taken. In each RB, NC (0.1 g, 0.06 mmol of anhydrous glucose units, DP = 100) obtained from pinewood (explained above) was taken with THF (10 ml), stirred for 1 h, and conducted freeze-vacuum-thaw cycles of the mixture three times. Triethylamine (0.2 mmol) and 4-dimethyl aminopyridine (0.24 mmol) were added to the mixture and conducted freeze-vacuum-thaw cycles three times. Three different amounts of Bbib (0.1, 0.2, and 0.4 mmol) were added to the three reaction mixtures in three portions over 10 min. The reaction mixtures were stirred under nitrogen for 24 h at 50°C. The reaction mixtures were filtered, and the solid was washed with chloroform and acetone. The three products obtained were named macroinitiator (A), (B), and (C), respectively. All the macroinitiators were analyzed for the Br group using ICP-MS. The product, macroinitiator (B), was analyzed using FTIR, and NMR.

4.2.5 | Grafting polymer from macroinitiator (NC-polymer synthesis)

The ATRP polymerization of monomer on cellulose was conducted according to the previously established method with some modifications.[13] Three reaction setups with macroinitiators of three different concentrations of Bibb groups were taken to obtain polymers with three different grafting densities. The rest of the reagents were taken in the same amount for all three reactions. Three reactions using the macroinitiators (A), (B), (C) (50 mg, which contains 0.008, 0.025, and 0.05 mmol of Br group, 1.4, 4, and 7.7 wt.% Br in macroinitiator as explained in Section 2.2.4) were conducted as follows: The macroinitiator was taken in an RB (RB-1) with DMSO (1 ml). To the RB-1, a sacrificial initiator, Ebib (2.4 mg, 0.012 mmol), was added and conducted Freeze-Vacuum-thaw cycles. The reaction mixture was kept stirring at

65°C under Argon gas. In another RB (RB-2), monomer (0.38 g, 1.28 mmol) was taken DMSO (3 ml), conducted freeze-vacuum-thaw cycles. To RB-2, CuBr (0.033 mmol) and PMDETA (0.033 mmol) were added, and continued stirring for 30 min. The material in RB-2 was taken in a degassed syringe and poured into RB-1 at 65°C. The reaction mixture was stirred for 24 h under Argon gas.

The reaction mixture was cooled and centrifuged. The supernatant liquid is separated from the precipitate. The supernatant liquid was passed through the alumina column to separate the copper catalyst, and then THF (10 ml) was added to the column eluted solution to precipitate the polymer (free polymer due to sacrificial initiator) and was washed with THF (20 ml) at 50°C and filtered. This product was analyzed in GPC.

The precipitated grafted NC on centrifugation was washed with THF (50 ml) and acetone (50 ml) using Soxhlet extraction.

The solid was dried in an oven. The three NC-polymer products obtained using macromolecules (A), (B), and (C) are named NC-polymerL, NC-polymer, and NC-polymerH, respectively.

The yield of NC-polymerL, NC-polymer, and NC-polymerH were 0.08, 0.13 and 0.21 g, respectively. The grafting ratio of polymer is calculated using the formula,

$$\text{grafting ratio} = [(W_2 - W_1)/W_1] \times 100, \quad (1)$$

where W_1 is the weight of the macroinitiator taken for reaction, W_2 is the NC-polymer yield. The grafting ratio of NC-polymerL, NC-polymer and NC-polymerH were calculated to be 60, 160, and 320%.

Grafting densities (with respect to the amount of monomer present in polymers) were analyzed using UV–vis spectroscopy and using a calibration curve made from the pure monomer. The sheet formed using NC-polymerL, NC-polymer, and NC-polymerH were used to find the effect of grafting densities on WVTR.

NC-polymer was characterized using NMR, FTIR, TGA, DSC, SEM, and UV–Vis analysis and further taken to analyze the photo responsiveness and the WVTR of the sheets made from the NC-polymer by varying the grammage and the crosslinking time of the sheet.

4.3 | Preparation of films using NC-polymer and NC

4.3.1 | NC-polymer membrane for studying photoresponsivity properties

NC-polymer (10 mg) was taken in DMSO (1 ml), and stirred overnight. Well-dispersed sample (30 μl) was pipetted out onto the quartz slide and air-dried. The prepared sample was named NC-polymer (quartz slide). The NC-polymer (quartz slide) was irradiated with a UV crosslinker for increasing time intervals, and the UV–Vis spectrum was recorded from 200–800 nm.

4.3.2 | NC-polymer sheets for WVTR, SEM, and contact angle measurement analysis

Samples of NC-polymer with 0.19, 0.28, and 0.38 g were made a slurry in DMSO to make 1% solution and filtered through filter paper to form a layer on filter paper with 40, 60, and 80 g/m^2 grammage, respectively. The sheets were air-dried overnight. To create well-dried sheets, the sheets were further dried in an oven at 40°C overnight. Each sheet with varying grammage was kept under a 365 nm UV crosslinker for varying time intervals (4, 8, 10, and 12 h) (as mentioned in Figure 7). Thus, sheets made of NC-polymer on filter paper, without irradiating with UV crosslinker and after irradiating with crosslinker were named NC-polymer-S and NC-polymer-S-CL, respectively. For SEM, FTIR, and contact angle analysis, NC-polymer-S and NC-polymer-S-CL (10 h) (crosslinking for 10 h) were prepared using 60 g/m^2.

A sheet made up of 0.28 g of NC-polymerL and NC-polymerH were also prepared in the same method explained above to prepare 60 grammage sheets. All the sheets with 60 grammage were analyzed for WVTR to study the effect of the grafting density on the WVTR of the sheets before and after UV crosslinking for 10 h.

4.3.3 | NC-polymer, NC membrane on silicon wafer for SEM analysis

Sample preparation for SEM analysis on silicon wafers was done by taking 1% NC-polymer in DMSO and then drop-casting 3 μl into two silicon wafers. Both silicon wafers were dried in an oven at 40°C overnight; one of them was kept in a UV crosslinker for 10 h. The samples were named NC-polymer (Silicon wafer), NC-polymer-CL (Silicon wafer).

The sample preparation of NC for SEM was done by diluting the sample to 1% in DMSO and pipetting 3 μl of the prepared sample onto a silicon wafer, followed by oven drying overnight. All the samples were coated with iridium for 2 nm thickness.

4.4 | Characterization method

FTIR spectroscopy was conducted using Agilent Cary 630. Solid-state ^{13}C NMR spectra were recorded at 25°C on a Bruker Avance spectrometer operating at a 52-degree magic angle at 75.4 MHz. The acquisition was performed with a standard cross-polarization pulse sequence (cp.av) at 5 kHz, recycling delay 4 s, contact time 2 ms, with an acquisition time of 20 ms and a spectral width of 50,000 Hz. A total of 24,000 transients were collected.

^{1}H NMR was recorded on Bruker DRX 400, using a d_6-DMSO solvent. Differential scanning calorimetry (DSC) analysis was done using the PerkinElmer DSC8000 system. Mettler TGA/DSC1 STAR system was used to analyze Thermogravimetric analysis (TGA) ranging from 40–900°C with a heating rate of 20°C/min under nitrogen. UV–Vis measurements were carried out using a UV-1800 Shimadzu spectrophotometer. The calibration curve for determining the grafting density (in terms of wt.% monomers) of NC-polymers were prepared using different concentrations of monomers in DMSO and analyzing the absorbance in UV–vis spectroscopy at 245 nm. 0.002 g/100 ml of the samples were prepared using NC-polymers in DMSO to analyze the grafting densities.

The amount of monomer in a known weight of polymer was calculated using the following formula:

$$\text{Wt.\%monomer in polymer} = [\text{monomer conc.}(\text{g}/100\,\text{ml}) \div \text{NC} - \text{polymer conc.}(\text{g}/100\,\text{ml})]100. \tag{2}$$

FEI Nova NanoSEM 450 was used to perform scanning electron microscopy (SEM). A field-emission source at 5 kV was used.

A UV crosslinker used for crosslinking coumarin molecules is UVP CL-1000, equipped with five Hitachi 8-WATT F8TS black light fluorescent tubes (broad band lamp), operating at 365 nm; made in Japan, supplied by ANL lighting, Australia. The fluence/power of irradiation is 95 W/m^2. Size exclusion chromatography (SEC) was conducted using the Tosoh High-Performance EcoSEC HLC-8320 GPC system, equipped with both refractive index and ultraviolet detectors (UV detection, at 280 nm). The analysis columns used for SEC were (TSKgel Alpha-4000 (400 Å pore size) and TSKgel Alpha2500 (125 Å pore size)) in series. The standard calibration curve was prepared using standard polystyrene solutions; DMF with 1% LiBr was used as the solvent.

Quantification of Br group in the macroinitiator and Cu in NC-polymer were done using ICP-MS, iCAP TQe QTEGRA instrument. The following method is used to prepare the sample for analysis.

Oven dried macroinitiator (2 mg) was taken in a standard flask with nitric acid (2 ml, 70%), sonicated for 5 min. The mixture was kept in a water bath at 60°C for 1 h, until all the solid dissolved in the solution. The standard flask was made up to the mark using deionized water. To find the Br group in macroinitiator, a known concentration of standard solutions is prepared using N-bromo succinimide. The percentage of Br group in the macroinitiator was calculated using the formula (3).

$$\%\text{Br content} = [\text{Br conc.}(\text{mg/L}) \div \text{macroinitiator conc.}(\text{mg/L})]100. \tag{3}$$

To find the amount of Cu present in NC-polymer, a known concentration of standard solutions is prepared using copper bromide. The percentage of Cu in NC-polymer was calculated using formula (4).

$$\%\text{Cu content} = [\text{Cu conc.}(\text{mg/L}) \div \text{NC} - \text{polymer conc.}(\text{mg/L})]100. \tag{4}$$

The water contact angle of NC-polymer-S and NC-polymer-S-CL (10 h) sheets were analyzed using DataPhysics, OCA35 instrument using 3 μl droplets. Every sheet was tested for five measurements at different points. The thickness of the sheets NC-polymer-S and NC-polymer-CL (10 h) were measured using an L&W Micrometer 51 at multiple points on a sheet. WVTR of NC-polymer-S and NC-polymer-S-CL (at 4,8,10 and 12-h irradiation) was measured using ASTM E96 wet-cup method[34] with the coating side toward the atmosphere at 23°C and 50% RH. The increase in mass with time was recorded, and the slope of the straight line was used to calculate the WVTR of the sheets in terms of g/m^2/day.

AUTHOR CONTRIBUTIONS

Poornima Vijay: Data curation (lead); formal analysis (lead); investigation (equal); methodology (equal); writing – original draft (lead); writing – review and editing (equal). **Warren Batchelor:** Methodology (supporting); supervision (equal); writing – review and editing (equal).

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DATA AVAILABILITY STATEMENT

The data supporting this study's findings are available in this article's supporting information. In addition, other raw experimental data is available on request.

ORCID

Kei Saito https://orcid.org/0000-0002-5726-8775

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