Supporting information

Dual responsive Curcumin loaded N-Isopropylacrylamide/Acrylated linseed oil copolymeric hydrogel films: Tuned LCST with value-added properties

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Materials

Linseed oil (L.O.) (α-linolenic acid 51.9-55.2 %, palmitic acid 7 %, stearic acid 3.4-4.6 %, oleic acid 18.5-22.6 %, linolenic acid 14.2-17 %) was purchased from HIMEDIA. Acrylic acid and $CDCl_3$ were procured from Sigma-Aldrich. Hydroquinone and N, N, N, N'-Tetramethyl ethylenediamine (TEMED) were obtained from TCI chemicals. 30 % w/v hydrogen peroxide (H_2O_2) was procured from Nice chemicals. Seralite SRC 120 was obtained from SRL Pvt. Ltd, India. Glacial acetic acid, sodium carbonate, sodium bicarbonate and sodium sulfate were procured from Merck.

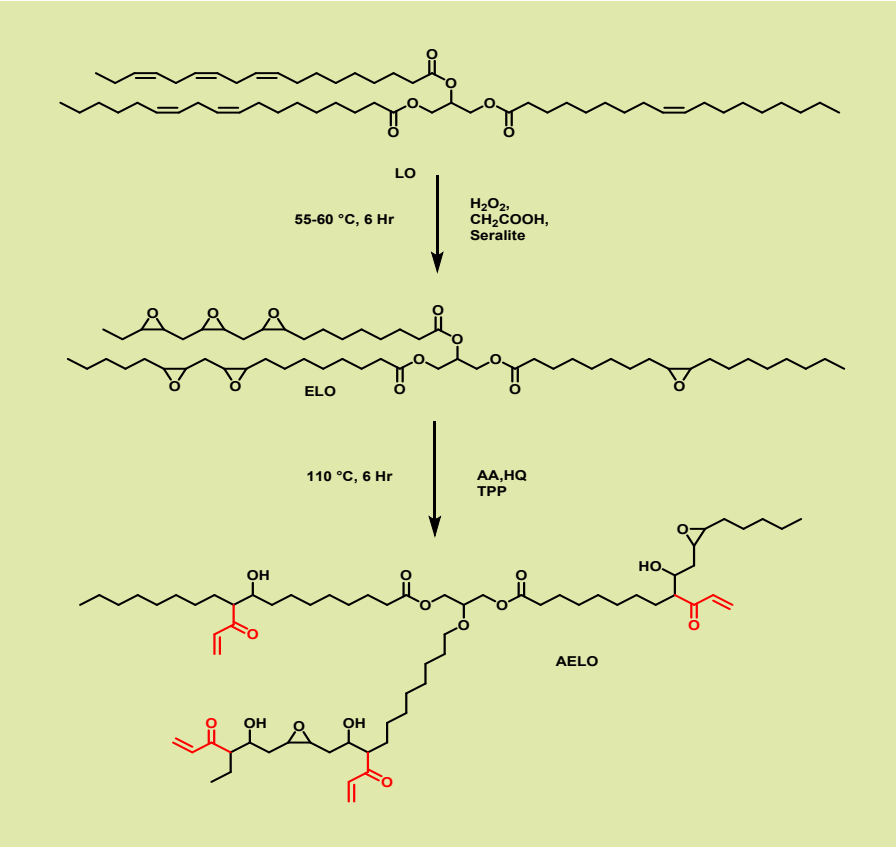
Experimental section

Synthesis of Acrylated epoxidized linseed oil (AELO)

Acrylated epoxidized linseed oil (AELO) was prepared via a two-step process reported by our group (**Scheme S1**)[1]. Initially, linseed oil was epoxidized employing Prilezhaev epoxidation. 79 g of linseed oil was added to the 3-neck round bottom flask connected with magnetic stirrer, followed by the addition of 30 g glacial acetic acid and seralite (19.75 g) mixture and stirred for 30 min. After this, 113 g of H_2O_2 was added using a dropping funnel, and then the reaction was carried out for 6 hr by maintaining the temperature between 55-60 °C. Afterward, the epoxidized layer was separated using filtration and washed with 2 wt.% Na_2CO_3 solution and then distilled water. Epoxidized linseed oil (ELO) was then passed through anhydrous sodium sulphate and dried using a vacuum oven.

For the acrylation process, 65 g of ELO and 0.5 wt. % hydroquinone were thoroughly mixed in a two-neck round bottom flask. 19.58 g of acrylic acid was introduced dropwise to the reaction media using a dropping funnel with continuous stirring. 1.23g (1.5 wt.% ELO+AA mixture) of triphenylphosphine was added as a catalyst. The reaction continued for 6 hr at 110 °C. Acrylated epoxidized linseed oil (AELO) was washed with 2 wt.% $NaHCO_3$ solution

and passed over anhydrous Na_2SO_4. Further drying of AELO was performed in a vacuum oven.



Scheme S1. Acrylation of epoxidized linseed oil

Characterization

^{1}H NMR spectrum was recorded using the 500 MHz Bruker Advance DPX spectrometer using $CDCl_3$ as solvent.

Results and discussion

Functional group analysis

ATR-FTIR and ^{1}H NMR (**Fig. S1**) are used to validate the formation of ELO and AELO. The typical peak associated with C-H stretching from LO's C=C-H at 3015 cm^{-1} is noticeably diminished in ELO, as shown in **Fig. S1**[1]. The peak at 1654 cm^{-1} attributed to C=C is not

prominent in ELO, confirming that LO had undergone epoxidation. The vibration seen at 822 cm^{-1} repeatedly confirms the epoxidation of linseed oil. The acrylate moiety's double bond in AELO is shown as a doublet at 1637 and 1619 cm^{-1}. The CH_2 scissoring vibration of CH_2=C in the acrylate group is represented by the peak at 1406 cm^{-1}. The peaks at 984 and 966 cm^{-1} and those at 1296 cm^{-1} and 1272 cm^{-1} are attributed to C-H scissoring vibration in acrylate CH=C and CH_2 rocking vibration of CH_2 in the acrylate groups, respectively[2,3].

Epoxidation and acrylation are further confirmed with ^{1}H NMR. The olefinic hydrogen atoms of double bond in LO. appeared at 5.3 ppm, which has significantly reduced in ELO. The characteristic peaks of -CH- protons from epoxide moiety occurred at 2.9-3.12 ppm in ELO, validating the epoxidation of LO. Three successive peaks at 5.8–6.5 ppm are seen after acrylation, and these peaks correspond to the three acrylate group protons in AELO[2,3]. Proton peaks corresponding to the epoxy ring observed in the AELO spectrum with reduced intensity suggest that complete acrylation is impossible. This might be due to the steric Sratio between the area of the epoxide peaks (^{1}H NMR) peak at 2.85-3.2 ppm and the area of the unsaturation bond peak, which appeared at 5.27–5.45 ppm, is used to calculate the degree of epoxidation, which was calculated to be 82 %. In a similar method, the degree of acrylation was calculated by dividing the area of the acrylate group by the sum of the areas of epoxy and acrylate, and it was calculated to be 56 %[4].

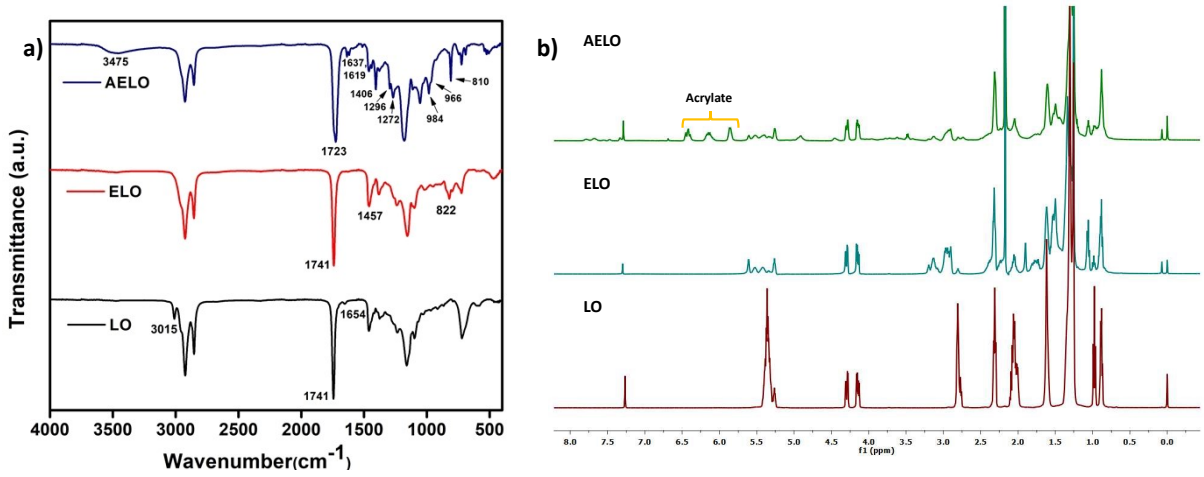
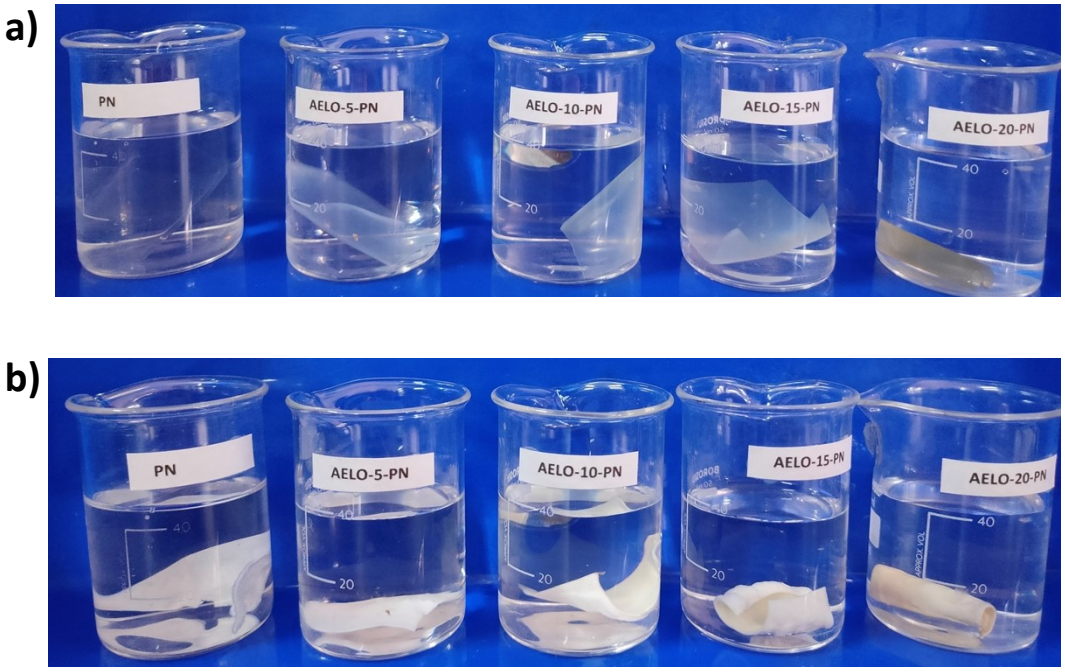
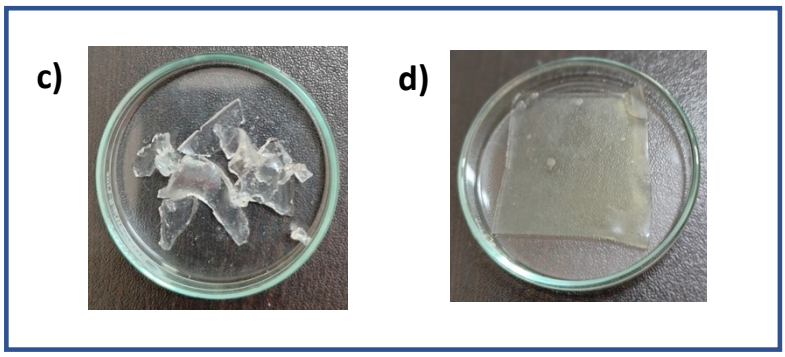


Fig. S1. a) ATR-FTIR comparison analysis and b) ^{1}H NMR analysis of LO., ELO and AELO

Swelling studies





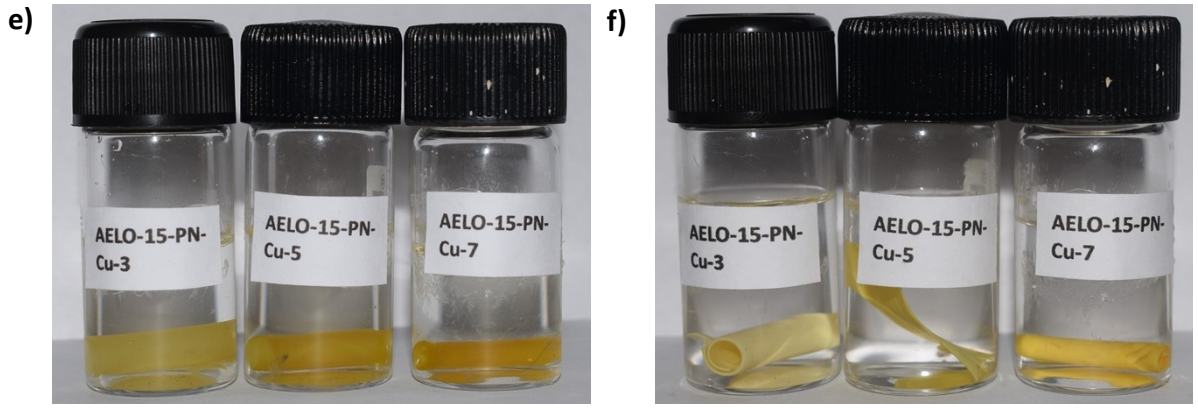


Fig. S2. (a) Images of the swelled samples at 27 °C and (b) at 40 °C (c) image of the PN. after equilibrium swelling and (d) image of the AELO incorporated sample after equilibrium swelling, (e) images of curcumin incorporated films at 27 °C and (f) at 40 °C

Table S1. Equilibrium swelling capacity of hydrogel films.

Sample	Equilibrium swelling at 27 °C (g/g)
PN	9.87±0.114
AELO-5-PN	4.50±0.089
AELO-10-PN	3.03±0.121
AELO-15-PN	2.28±0.091
AELO-20-PN	1.36±0.098
AELO-15-PN-Cu-3	1.02±0.009
AELO-15-PN-Cu-5	0.82±0.009
AELO-15-PN-Cu-7	0.72±0.011

DMA Analysis

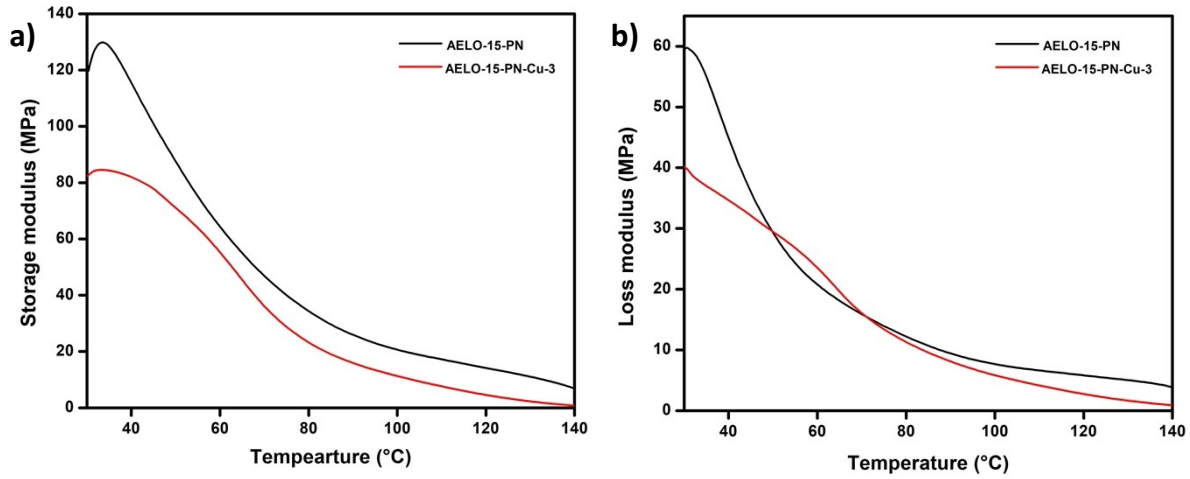


Fig. S3. Comparison of (a) storage and (b) loss modulus of AELO-15-PN and AELO-15-PN-Cu-3

Colour changes with different pH

Table S2: Colour parameter analysis

	Dry sample			pH 4			pH 7.4			pH 9.2		
	L	**a**	**b**	**L**	**a**	**b**	**L**	**a**	**b**	**L**	**a**	**b**
AELO-15-PN-Cu-3	81.82	-6.69	44.79	82.68	-4.29	39.43	80.6	-2.23	36.79	77.46	2.4	40.53
AELO-15-PN-Cu-5	80.57	-5	64.52	80.81	-3.43	62.04	73.92	1.33	61.01	66.98	12.32	61.02
AELO-15-PN-	74.44	6.4	74.81	73.9	4.05	73.63	66.34	14.14	58.73	57.37	24.58	53.82

Cu-7

References

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