Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information

Non-toxic layered double hydroxide nanoplatelet dispersions for gas barrier coatings on flexible packaging

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Table of contents

1. General details.

1.1. Analytical techniques for LDH characterisation

X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) results were investigated by using a PANalytical X'Pert Pro diffractometer in diffraction mode operating at a voltage of 40 kV and a current intensity of 40 mA with Cu-Kα radiation (λ = 1.5406 Å). LDHs and LDOs powder were placed into stainless steel sample holders.

20 μL of reconstructed LDHs dispersion and coating mixture were cast on a silicon wafer, dried at room temperature before placing into the sample holder, data was collected from 3 to 70°.

A 1° slit was used in both cases. Bragg diffraction due to sample holder were observed at 2θ = 43 – 44° and 50° and from silicon wafer were located at 2θ = 33°, 62° and 69°.

Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra of samples were recorded on Thermo Scientific Nicolet iS5 FTIR spectrometer in attenuated total reflectance (ATR) mode. Spectra were obtained in the range of 600 – 4000 cm^{-1}; 50 scans with 4 cm^{-1} resolution.

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was conducted at the Research Complex at Harwell on JEOL JEM-2100 TEM equipped with LaB6 filament at an accelerating voltage of 200 kV. Prior to analysis, samples were diluted with deionised water and sonicated in deionised water for 15 minutes. A few droplets of the resulting suspension were left to dry on a copper grid covered with a carbon film (300 mesh, Agar scientific).

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was carried out at the Research Complex at Harwell on a JSM-6610LV low vacuum fitted with EDX spectrometer at an accelerating voltage of 20 kV. Samples were mounted on adhesive carbon tape attached to aluminium stubs then sputter-coated with a 10 nm layer of platinum using a Quorum Q150T ES Sputter Coater to facilitate image.

Zeta potential and Dynamic light scattering (DLS) measurements

Zeta potential measurements and DLS analysis were carried out at the Begbroke Science Park, Department of Materials, University of Oxford. LDH Samples were dispersed and sonicated in deionised water at 0.1 wt% for 15 minutes before measurement. The resulting suspension samples were filled in a folded capillary cell and directly measured by using a using a Malvern Zetasizer Nano ZS.

Elemental analysis (EA)

Elemental C, H, N analysis was performed by a quantitative oxidative combustion technique by Mr Stephen Boyer at London Metropolitan University.

Inductively coupled plasma mass spectrometer (ICP-MS)

Mg and Al content were determined by ICP-MS analysis by Dr. Alaa Abdul-Sada at the University of Sussex on an Agilent 7500 Series ICP-MS in helium collision mode. Approximately 20 mg of samples were digested in 10 mL of 10% nitric acid solution. These solutions were then diluted by a factor of 100 with dilute nitric acid prior to analysis. Each solution was analysed three times and the data averaged.

Oxygen transmission rate measurement

Films are tested for oxygen transmission rate (OTR) using an oxygen permeation analyser (Systech Illinois Inc., Oxygen Permeation Analyser 8001) at 23 °C and 0% RH. OTR is recorded after a steady state permeation is reached and reported in units of $cc \cdot m^{-2} \cdot day^{-1}$.

Optical properties of coated films

All optical properties were tested at Product Technology Development Center (PTDC), SCG Packaging PLC, Ratchaburi, Thailand. Each sample was tested at least five times, average and standard deviation values were reported.

All thickness measurements are tested by using a thickness tester (Thwing-Albert Instrument Company, ProGage Thickness Tester). Average of ten measurements is reported in units of micron.

The transmittance of the coated and uncoated substrates was assessed by a haze meter (The haze-gard I, BYK-Gardner GmbH Inc) according to ASTM D 1003. It is the ratio of transmitted light to the incident light, which is influenced by the absorption and diffraction properties of the materials. The specimen is placed at the film holder at the entrance port of the haze meter in order to measure the transmittance. Average of ten measurements is reported in units of percent.

The clarity of the coated and uncoated substrates was assessed by a haze meter (the haze-gard I, BYK-Gardner GmbH Inc). This measurement describes how well very fine details can be seen through the specimen. It needs to be determined in an angle range smaller than 2.5 degrees. The specimen is placed at the film holder at the entrance port of the haze meter in order to measure the clarity. An average of ten measurements is reported in units of percent.

1.2. Starting materials and chemicals

$Mg(NO_3)_2 \cdot 6H_2O$ (AR), $Al(NO_3)_3 \cdot 9H_2O$ (AR), NaOH (AR), Na_2CO_3 (AR), urea, sodium docecylsulfate, lauric acid, stearic acid, amino acids (glycine, β-alanine, β-aminobutyric acid, β-leucine, β-phenylalanine, γ-aminobutyric acid, serine, asparagine, aspartic acid, and glutamic acid), sodium lactate, ethylene diamine, oxalic acid, glucose, PVA polymers (Mowiol 4-98, Mowiol 10-98, Mowiol 20-98, Mowiol 4-88, Mowiol 8-88 and Mowiol 18-88), and all solvents were purchased from Sigma-Aldrich Co. LLC., and used without further purification. Deionised water was used throughout the experimental processes.

1.3 Experimental details

Synthesis of LDHs

Synthesis of rosette shape like $Mg_4Al\text{-}CO_3$ LDHs *via* co-precipitation method

$Mg_4Al\text{-}CO_3$ LDHs rosette shape was synthesised following the procedure: the mixed metal salts solution of $Mg(NO_3)_2{\cdot}6H_2O$ (80 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (20 mmol) in 50 mL deionised water was added dropwise into 50 mL of 25 mmol Na_2CO_3 solution while stirring for 1 hour. Constant pH of 10 was maintained by addition of 4 M NaOH to the reaction mixture using an auto-titrator (Syrris, Atlas Syringe Pump) at feeding rate of 5 mL/min. After stirring at room temperature for 24 hours, the product was filtered and washed with deionised water until the pH was close to 7. Then, the wet cake was re-dispersed in 100 mL of deionised water. The wet cake was rinsed with 500 mL of ethanol then re-dispersed and stirred in 300 mL of this solvent at room temperature for 4 hours. The solvent was removed by filtration and the obtained LDH was further rinsed by 200 mL of this solvent. The product was dried in the vacuum oven overnight. The product washed with water was noted as Cop-W LDHs while the one treated with ethanol noted as Cop-AMO LDHs.

Synthesis of platelet shape $Mg_4Al\text{-}CO_3$ LDHs *via* urea hydrothermal method

$Mg_4Al\text{-}CO_3$ LDH platelet shape was synthesised following the procedure in: an aqueous solution of $Mg(NO_3)_2{\cdot}6H_2O$ (40 mmol), $Al(NO_3)_3{\cdot}9H_2O$ (10 mmol) and urea (160 mmol) in 100 mL deionised water was prepared. The solution was transferred to a Teflon-lined autoclave and heated in an oven at 100 °C for 24 hours.after the reactions were cooled to room temperature, the precipitated products were washed several times with deionised water by filtration and treated with ethanol using the same procedure mentioned above and the product was noted as UHT-AMO LDHs.

Calcination and reconstruction of LDHs

LDHs powder was transferred to the crucible and calcined in a furnace at 450 °C for 12 hours. After cooling, the calcined product, LDOs, was kept in a seal vial and used within days.

0.2 g of LDO powder was added to 2.66 mmol of selected organic solution in 2 mL of deionised water. The mixture was heated at 80 °C in a round bottom flask for 24 hours. Alternatively, the reaction was performed in an autoclave reactor. Then the reaction was cooled down to room temperature naturally. The obtain product was washed with deionised water by centrifugation three times and used without drying. Unwashed product was also compared. The final solid content of product was determined before use in the next step.

The organic molecules used in this study are amino acids (glycine, β-alanine, β-aminobutyric acid, β-leucine, β-phenylalanine, γ-aminobutyric acid, serine, asparagine, aspartic acid, and glutamic acid).

Barrier coating performance of LDHs with nanoplatelets from amino acid reconstruction

The amino acid-modified LDHs were mixed with an aqueous solution of PVA to yield a coated mixing of 5 wt% solids. The ratio of amino acid-modified LDH to PVA within the coating mixture was 70/30, 50/50 or 40/60.

Coated films preparation

The coating solution is applied to 23 μm thick corona-treated polyethylene terephthalate substrate (SARAFIL Transparent TF101, Polyplex Thailand), which is supplied by SCG Packaging PLC, by a Mayer rod coater and an automatic coater (K101, RK Print Coat Instruments Ltd.) equipped with a close wound rod having wire diameter of 0.08 mm. The substrate film is secured in the middle of the coating area and the rod is placed on the upper top of the film. Approximately 1-2 mL of the prepared coating solution is applied in the gap between the rod and the substrate along the width of the substrate. A Mayer rod moves down the substrate with a controlled speed and the coated film is obtained. All coated samples are dried naturally at room temperature. Coating thickness is controlled by using a yellow rod and fixing speed of the coater at #7 for all coatings.

2. Supplementary experimental data

Solubility data of compounds

Table S1. Summary of amino acid types used in this study.

Amino Acid Type	Amino Acid	Solubility in water (g/L)
Amino acid with nonpolar side chain	Glycine	250
	β-Alanine	545
	β-Leucine	24.26
	β-Phenylalainine	27
	β-Aminobutyric acid	1000
	γ-Aminobutyric acid	1300
Amino acid with polar side chain	Serine	425
	Asparagine	29.4
	Aspartic acid	4.5
	Glutamic acid	7.5

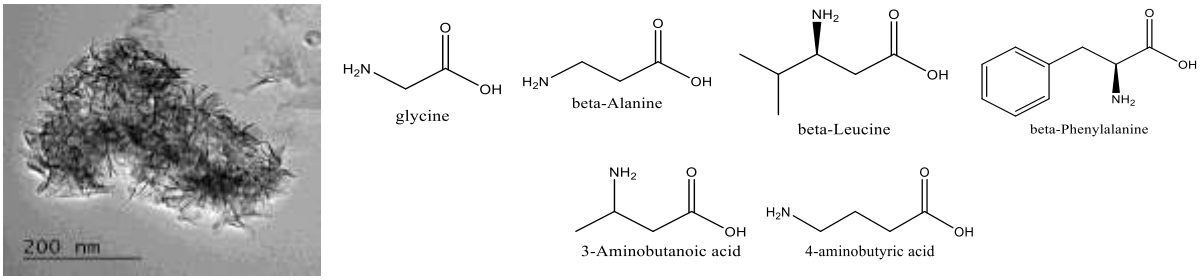


Fig. S1. TEM image of Cop-AMO LDHs before calcination and reconstruction and structure of nonpolar amino acids used in this study.

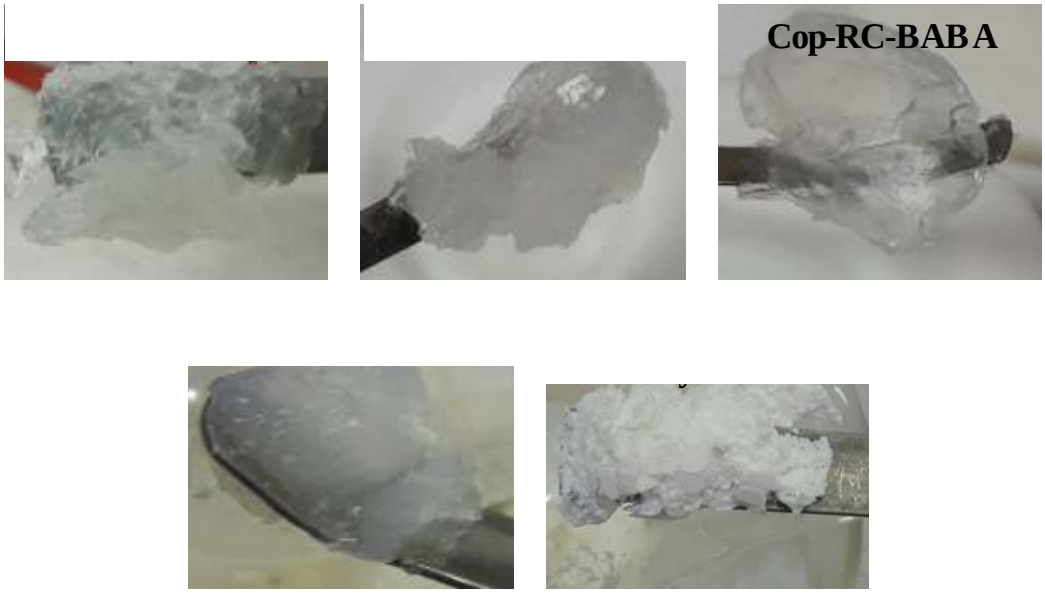


Fig. S2. Appearance of Cop-RC-amino acids by reconstruction with non-polar amino acids.

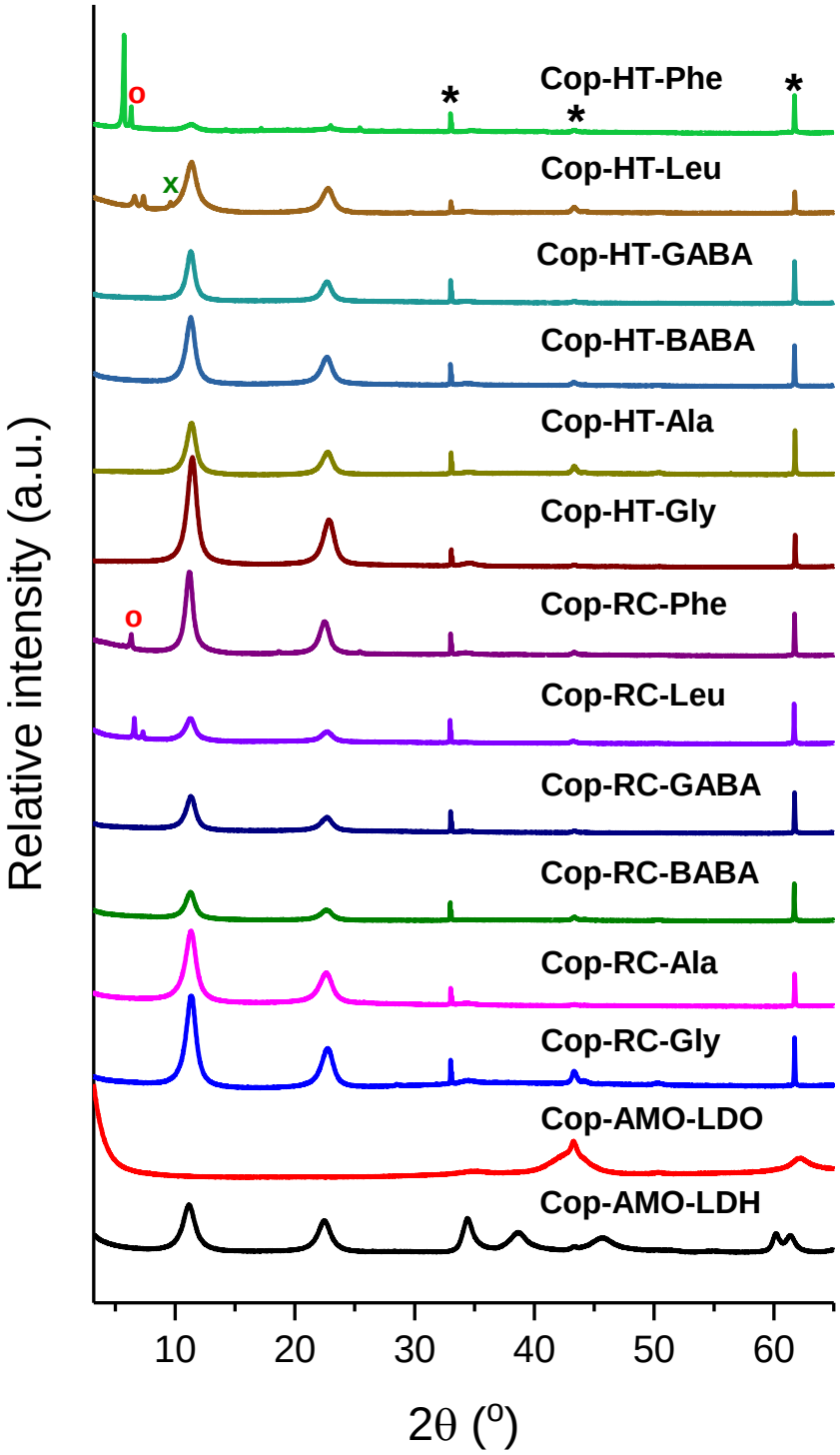
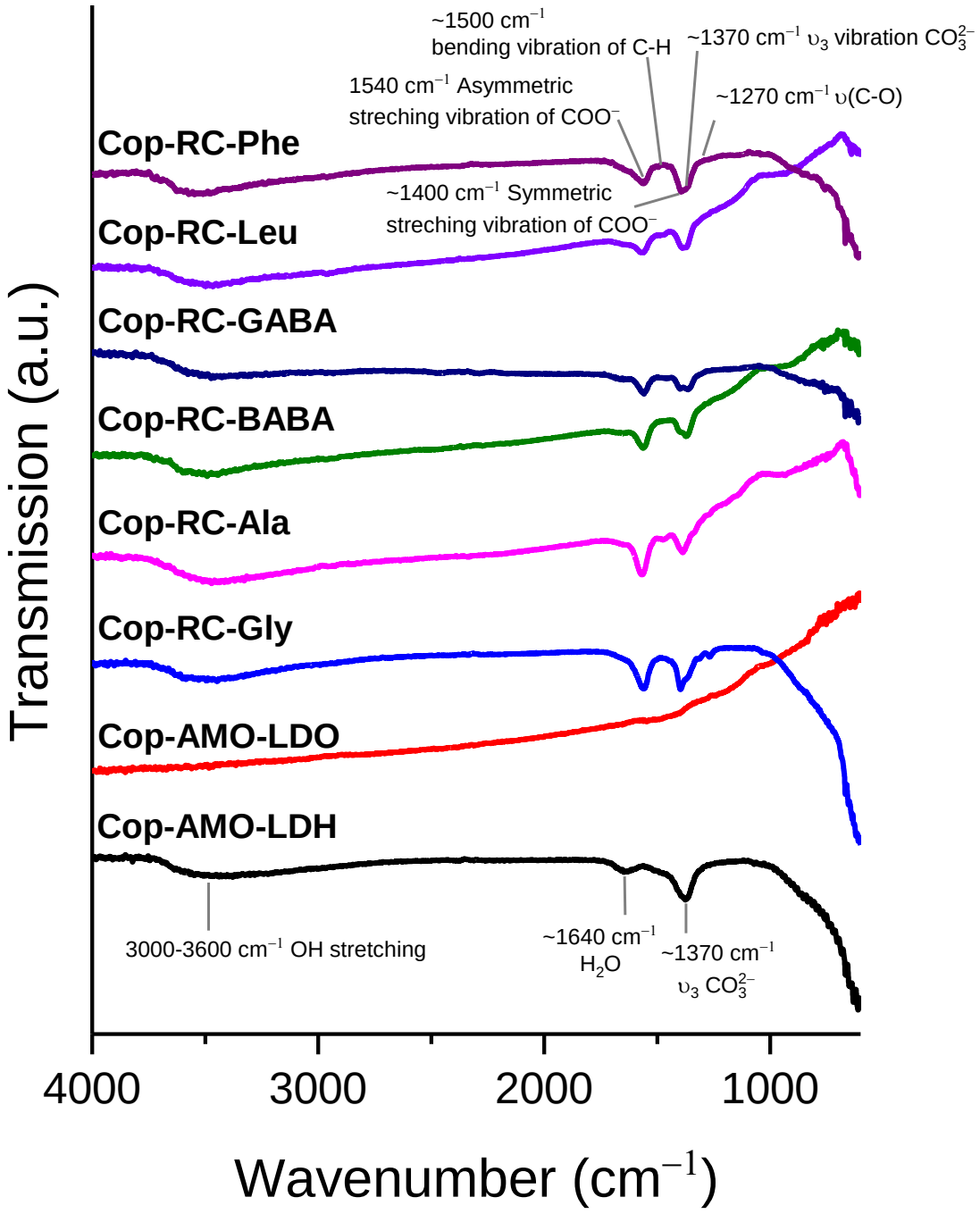


Fig. S3 XRD pattern of Cop-RC-amino acids and Cop-HT-amino acids by reconstruction with nonpolar amino acids. **o** and **x** denote the Bragg diffraction by impurities from phenylalanine (**o**) and leucine (**x**). (*Bragg diffraction due to the sample holder were observed at 2θ = 43-44° and 50° and diffraction from the silicon wafer were located at 2θ = 33° and 62°.)

Table S2. Summary of *interlayer* spacing of Cop-RC-amino acids and Cop-HT-amino acids using different nonpolar amino acids. 'RC' and 'HT' were denoted as product from an oil bath heated and hydrothermal conditions, respectively.

Sample	***Interlayer* spacing (Å)**
Cop-AMO LDHs	7.93
Cop-RC-glycine	7.78
Cop-RC-β-alanine	7.8
Cop-RC-β-aminobutyric acid	7.83
Cop-RC-γ-aminobutyric acid	7.8
Cop-RC-β-leucine	7.83, 12.05, 13.41
Cop-RC-β-phenylalanine	7.9
Cop-HT-glycine	7.71
Cop-HT-β-alanine	7.76
Cop-HT-β-aminobutyric acid	7.82
Cop-HT-γ-aminobutyric acid	7.83
Cop-HT-β-leucine	7.76, 12.02
Cop-HT-β-phenylalanine	7.79, 13.91, 15.43


~1500 cm⁻¹
bending vibration of C-H
~1370 cm⁻¹ υ3 vibration CO3 2–
1540 cm⁻¹ Asymmetric
streching vibration of COO⁻
~1270 cm⁻¹ υ(C-O)
~1400 cm⁻¹ Symmetric
streching vibration of COO⁻
Cop-RC-Phe
Cop-RC-Leu
Cop-RC-GABA
Cop-RC-BABA
Cop-RC-Ala
Cop-RC-Gly
Cop-AMO-LDO
Cop-AMO-LDH
3000-3600 cm⁻¹ OH stretching
~1640 cm⁻¹
H2O
~1370 cm⁻¹
υ3 CO3 2–
Transmission (a.u.)
4000
3000
2000
1000
Wavenumber (cm⁻¹)

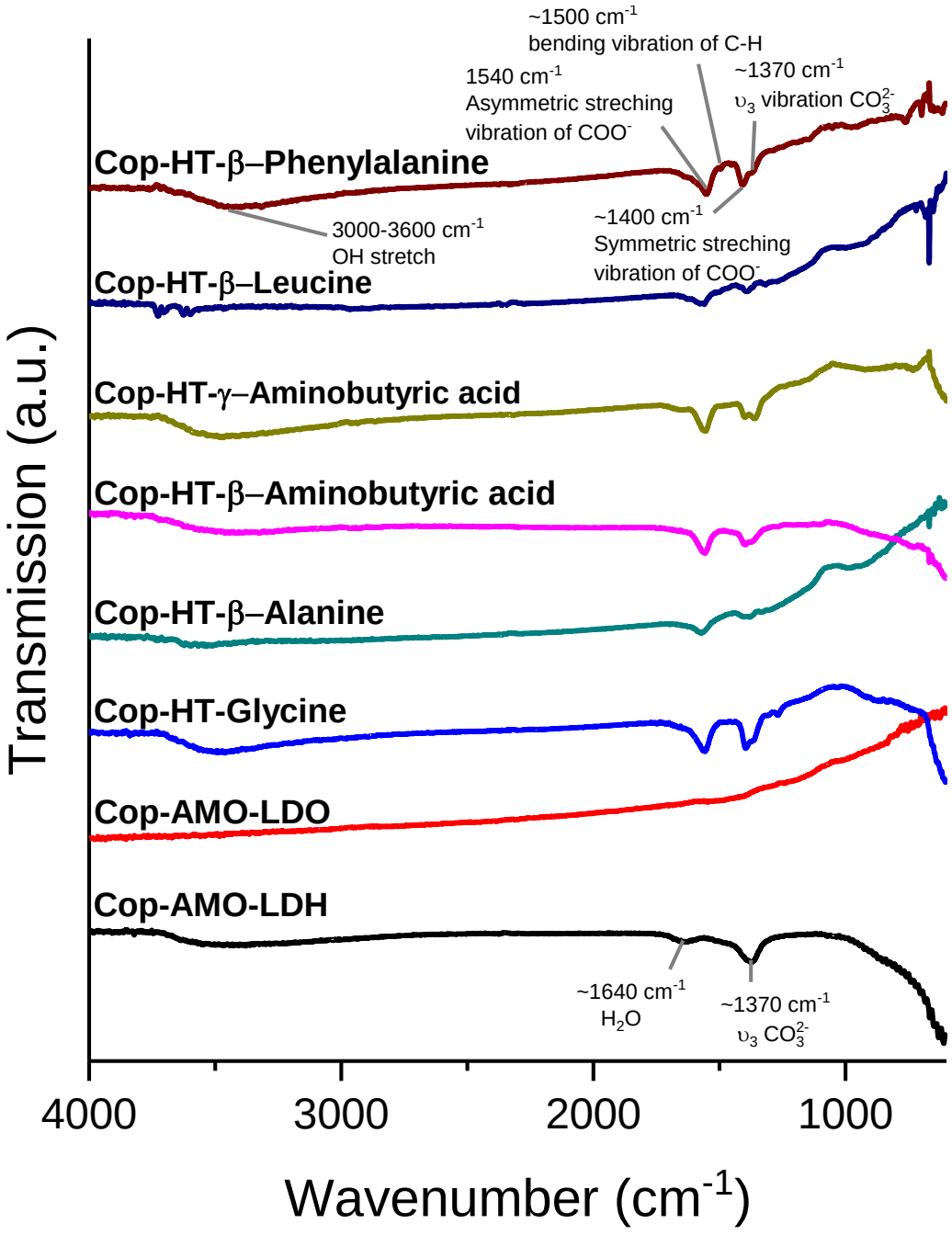


Fig. S4. FTIR spectra of Cop-RC-amino acids and Cop-HT-amino acids by reconstruction with nonpolar amino acids.

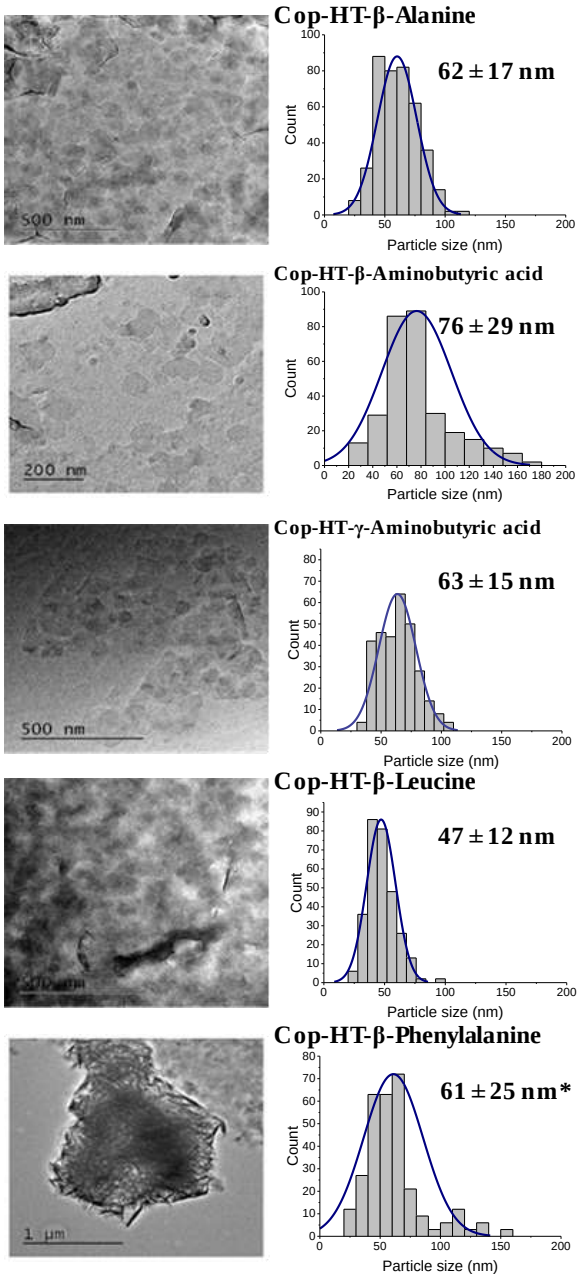


Fig. S5. TEM images with particle diameter distributions of Cop-HT-amino acids by reconstruction with nonpolar amino acids. Navy lines indicate the best fit of a Gaussian distribution, showing approximately a normal distribution. Mean values and standard deviation were obtained from measurement of 300 particles. '*' indicates that only small size particles were plotted the size distribution curves.

Table S3. Summary of average platelet diameter of Cop-RC-amino acids and Cop-HT-amino acids by reconstruction with nonpolar amino acids

Sample	Platelet Diameter
Cop−AMO LDHs	1131±504 nm*
Cop-RC-Glycine	42±12 nm
Cop-RC-β-Alanine	55±10 nm
Cop-RC-β-Aminobutyric acid	55±13 nm
Cop-RC-γ-Aminobutyric acid	52±15 nm
Cop-RC-β-Leucine	61±16 nm
Cop-RC-β-Phenylalanine	181±78 nm
Cop-HT-β-Alanine	62±17 nm
Cop-HT-β-Aminobutyric acid	76±29 nm
Cop-HT-γ-Aminobutyric acid	63±15 nm
Cop-HT-β-Leucine	47±12 nm
Cop-HT-β-Phenylalanine	61±25 nm, 0.5-1 μm

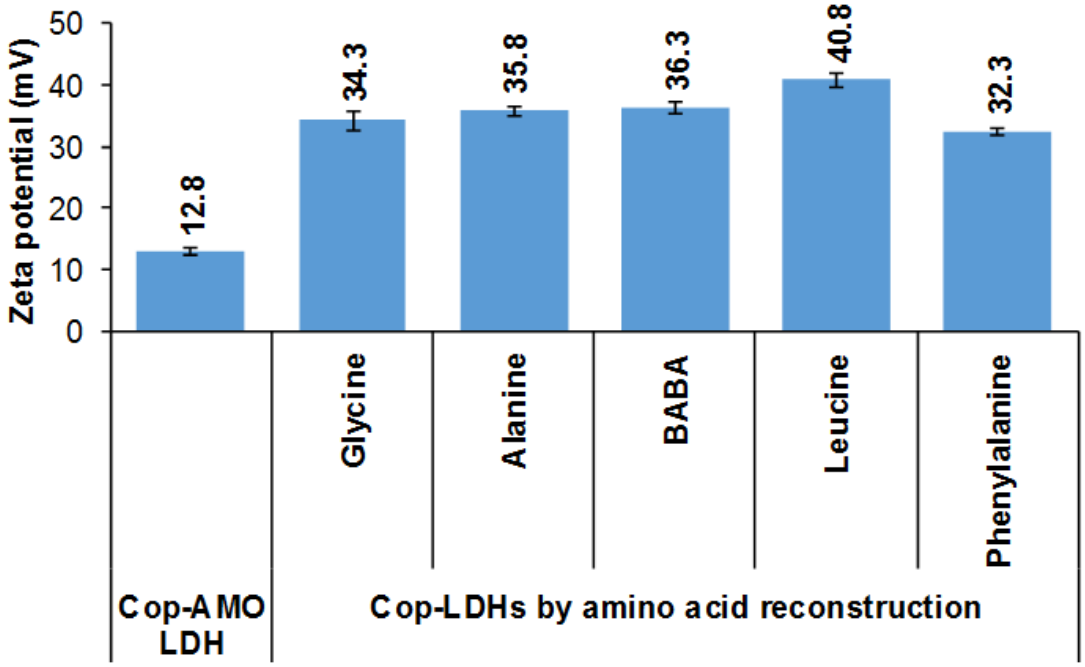


Fig. S6. Zeta potential of Cop-RC-amino acids by reconstruction with nonpolar amino acids.

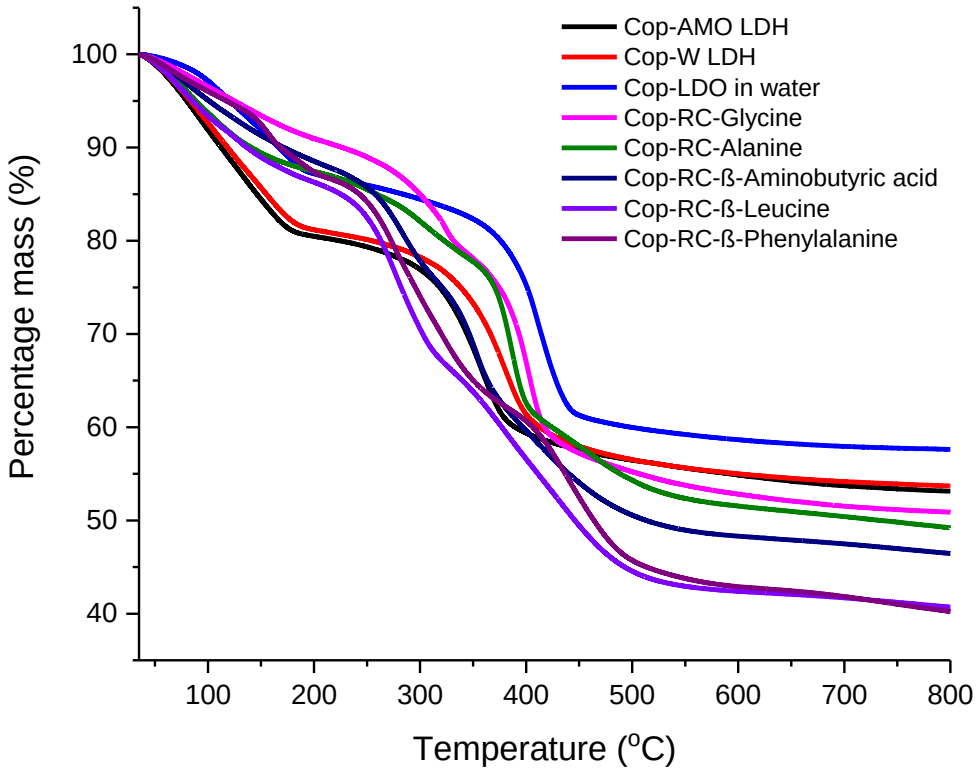


Fig. S7. TGA curves of Cop-RC-amino acids by reconstruction with nonpolar amino acids.

Table S4. Elemental analysis (EA) and TGA studies.

Sample	%Amino acid*	%C apart from amino acid*	%H apart from amino acid*	%Mass different from 'original LDH'**	%Mass different from 'controlled sample'**
Cop-AMO LDH	-	3.50	4.35	-	−4.50
Cop-LDO in water	-	1.46	4.29	4.50	-
Cop-RC-Glycine	16.67	0.06	2.33	−2.24	−6.74
Cop-RC-β-Alanine	27.56	0.53	4.43	−3.97	−8.47
Cop-RC-β-Aminobutyric acid	22.46	0.00	2.81	−6.73	−11.23
Cop-RC-β-Leucine	32.43	0.01	2.99	−12.54	−17.04
Cop-RC-β-Phenylalanine	38.82	3.98	2.28	-13.10	−17.60

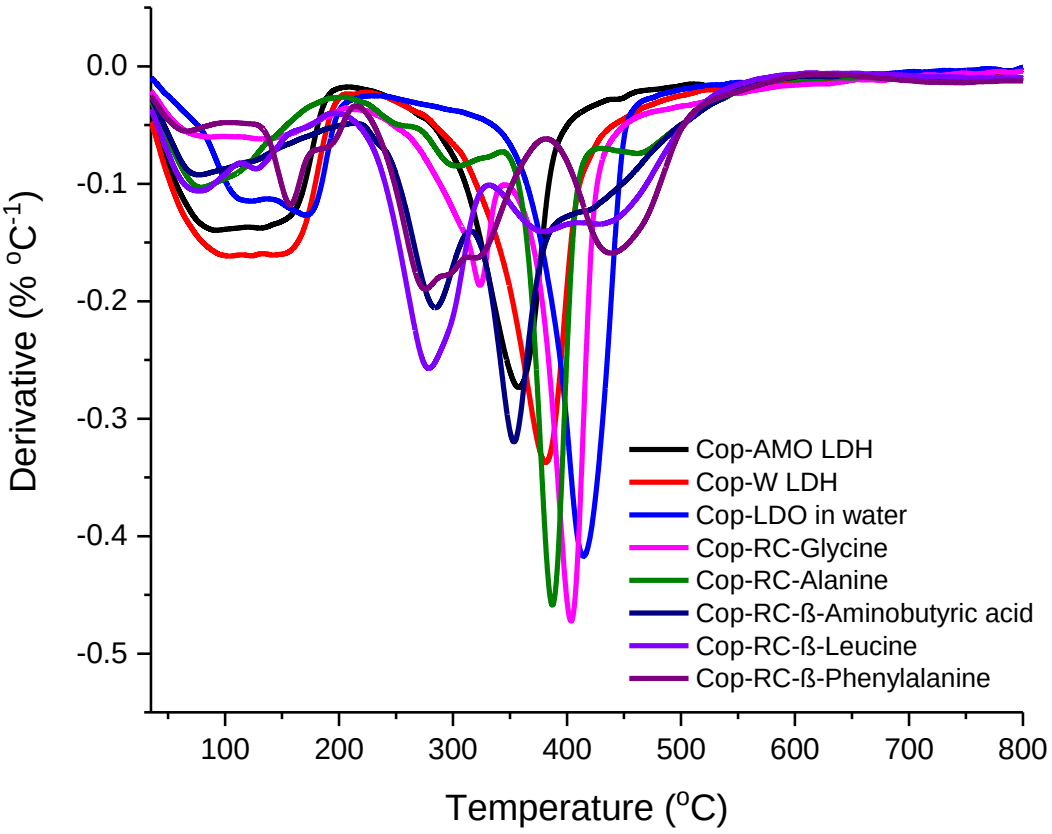


Fig. S8 Differential thermogravimetric curves (DTG) of Cop-RC-amino acids by reconstruction using nonpolar amino acids.

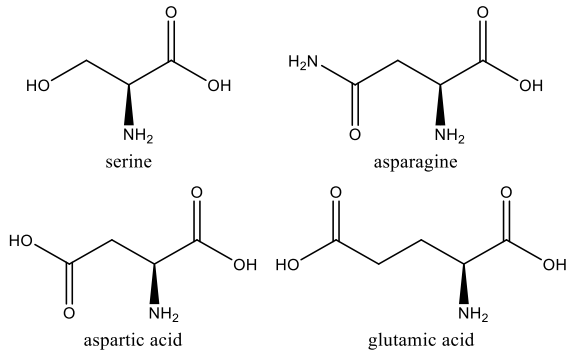


Fig. S9. Structures of the polar amino acids used in this study.

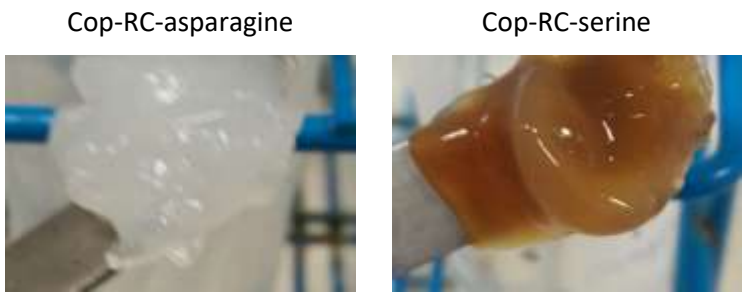


Fig. S10. Appearance of Cop-RC-asparagine and Cop-RC-serine.

Fig. S11. Dispersion of Cop-RC-amino acids by reconstruction with polar amino acids in water.

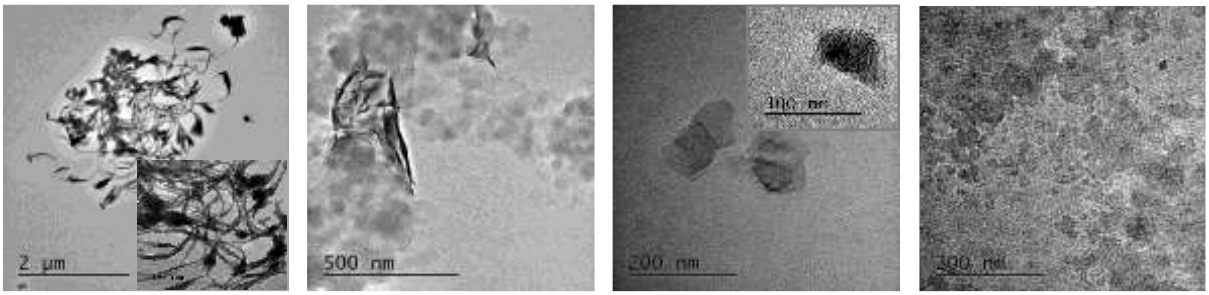


Fig. S12. TEM images of Cop-RC-amino acids by reconstruction using different polar amino acids.

Table S5. Summary of interlayer spacings and average platelet diameter of Cop-RC-amino acids using polar amino acids. The mean values and standard deviations by measurement of 300 particles from TEM images.

Sample	Interlayer spacing / (Å)	Platelet diameter/ (nm)
Cop-RC-aspartic acid	7.60	46±13
Cop-RC-glutamic acid	7.60	59±25
Cop-RC-asparagine	7.74	63±27
Cop-RC-serine	7.74	25±5

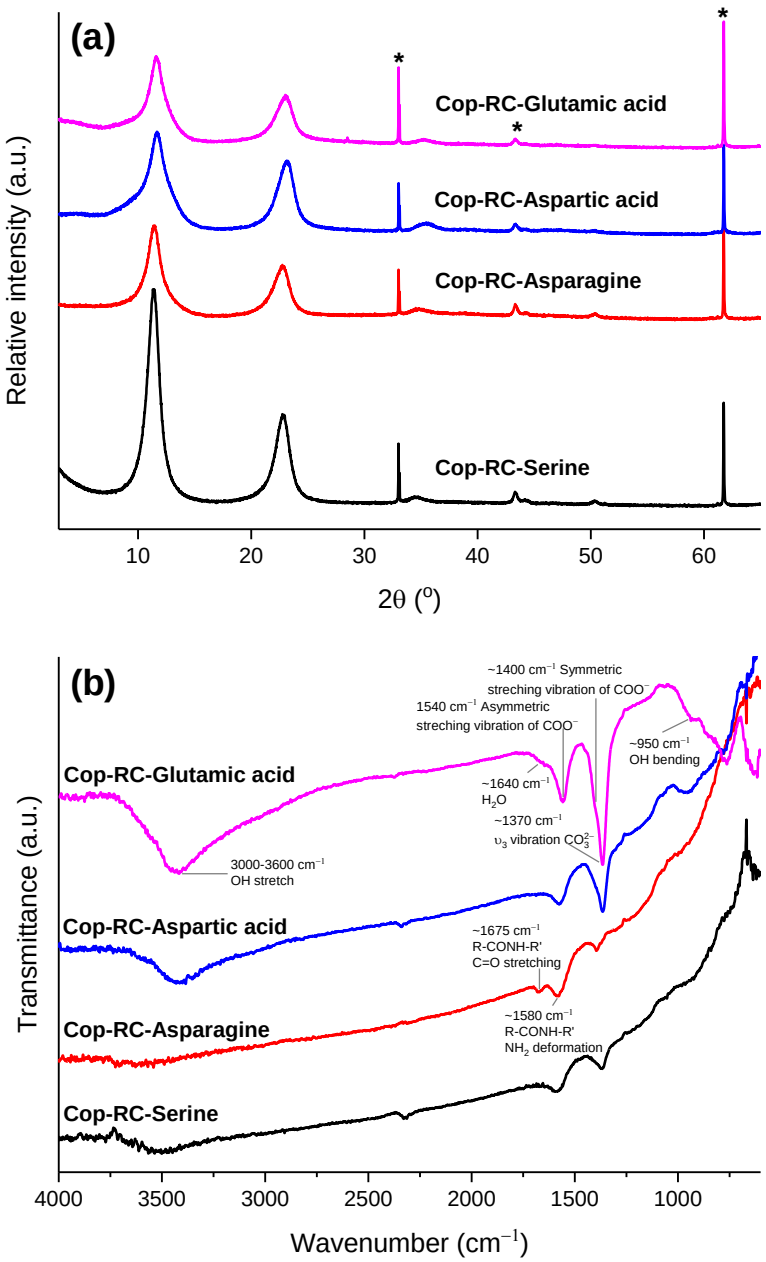


Fig. S13. (a) XRD patterns and (b) FTIR of Cop-RC-amino acids by recontruction using polar side chain amino acids. (*Bragg diffraction due to the sample holder were observed at 2θ = 43-44° and 50° and diffraction from the silicon wafer were located at 2θ = 33° and 62°.)

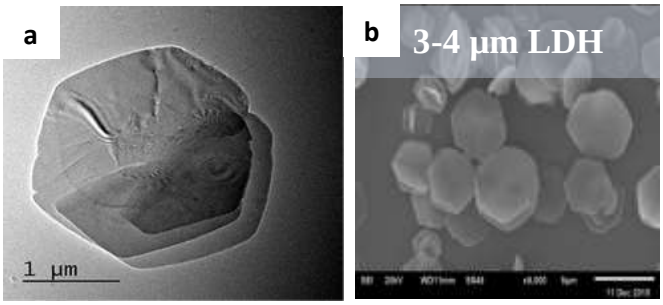


Fig. S14. (a) TEM and (b) SEM images of UHT-AMO LDHs

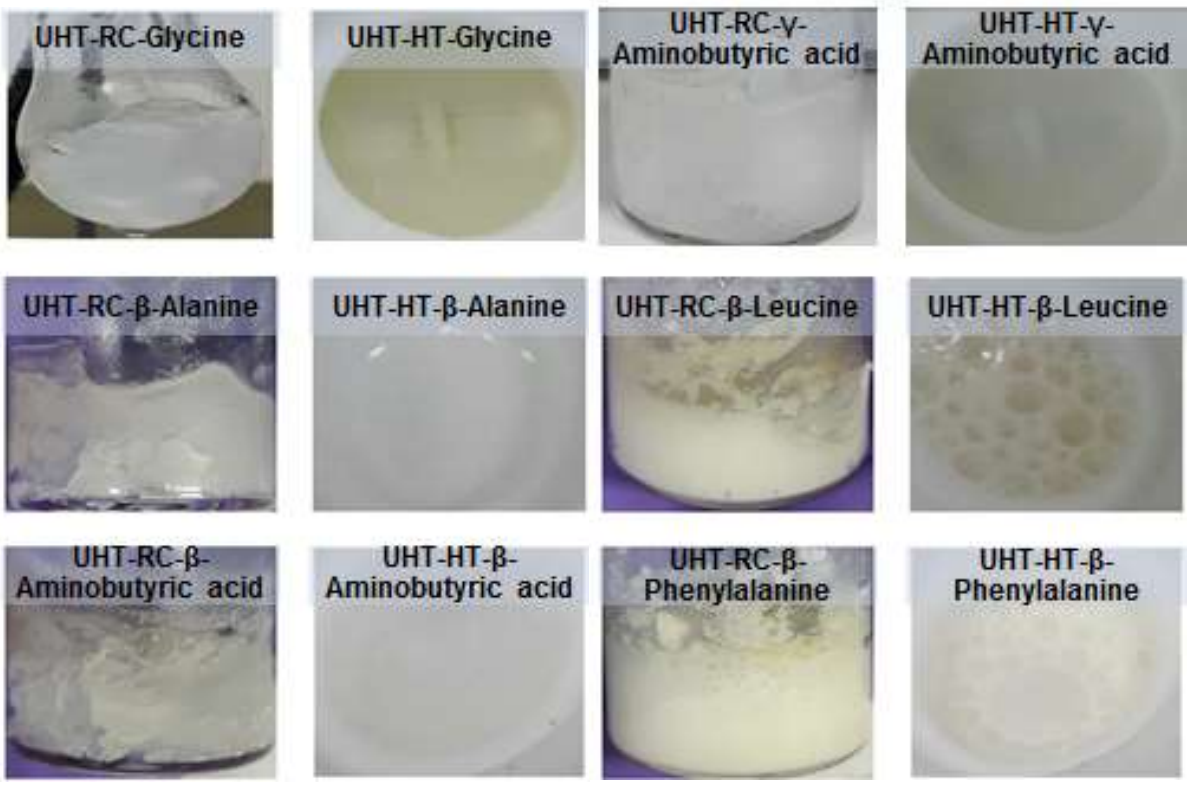


Fig. S15. Appearance of UHT-RC-amino acids and UHT-HT-amino acids by recontruction using non-polar amino acids.

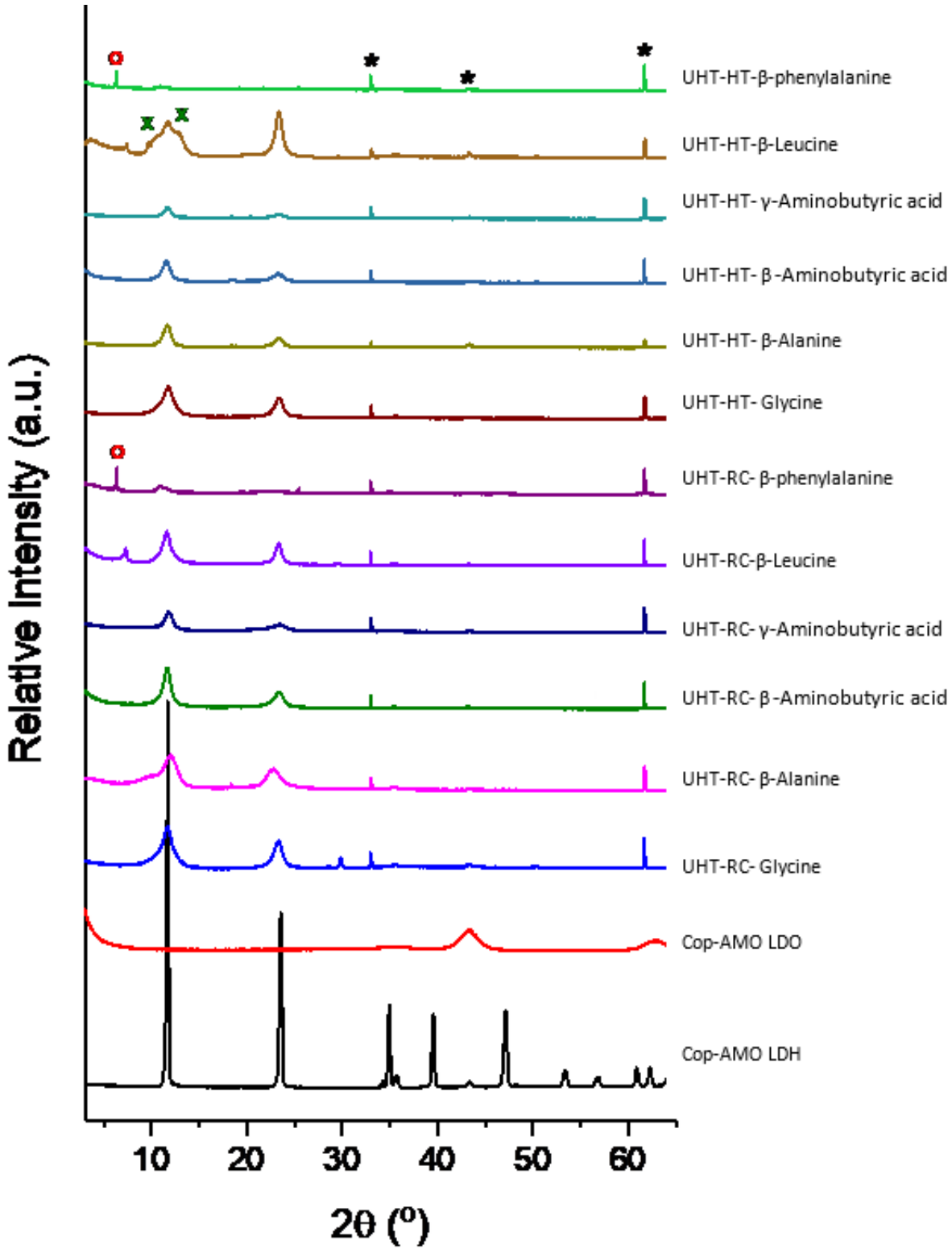


Fig. S16. XRD patterns of UHT-RC-amino acids and UHT-HT-amino acids by recontruction using nonpolar amino acids by nonpolar amino acids. **o** and **x** denote the Bragg diffractions of impurities from phenylalanine (**o**) and leucine (**x**). (*Bragg diffractions due to the sample holder were observed at 2θ = 43-44° and 50° and diffractions from the silicon wafer were located at 2θ = 33° and 62°.)

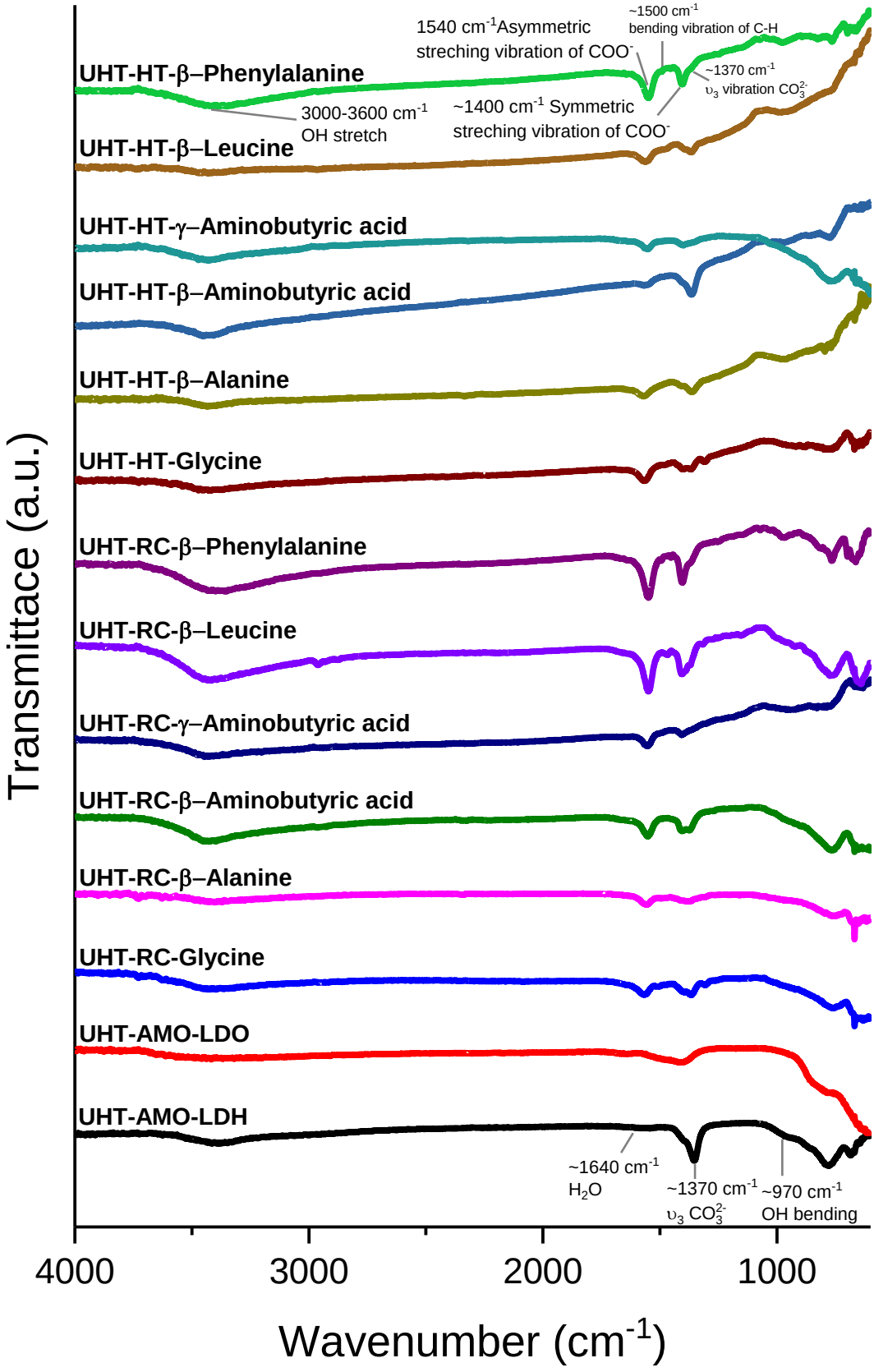


Fig. S17. FTIR spectra of UHT-RC-amino acids and UHT-HT-amino acids by recontruction using nonpolar amino acids.

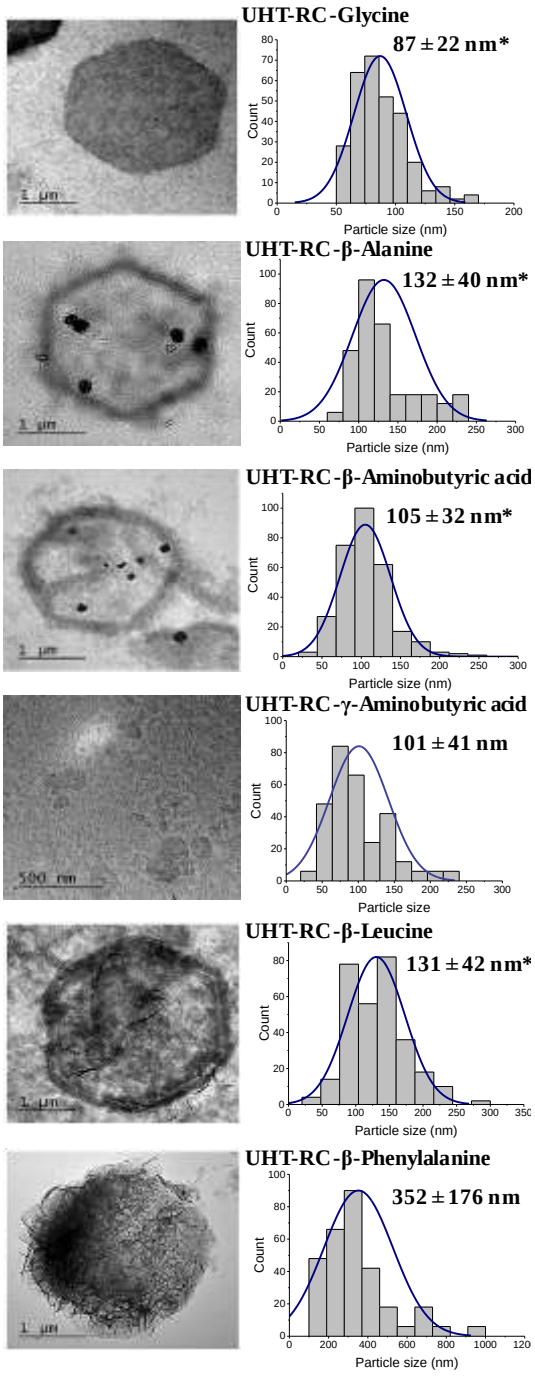


Fig. S18. TEM images with particle size distributions of UHT-RC-amino acids by recontruction using nonpolar amino acids. Navy lines indicate the best fit of a Gaussian distribution, showing approximately a normal distribution. Mean values and standard deviation were obtained from measurement of 300 particles. '*' indicates that only small size particles were plotted the size distribution curves.

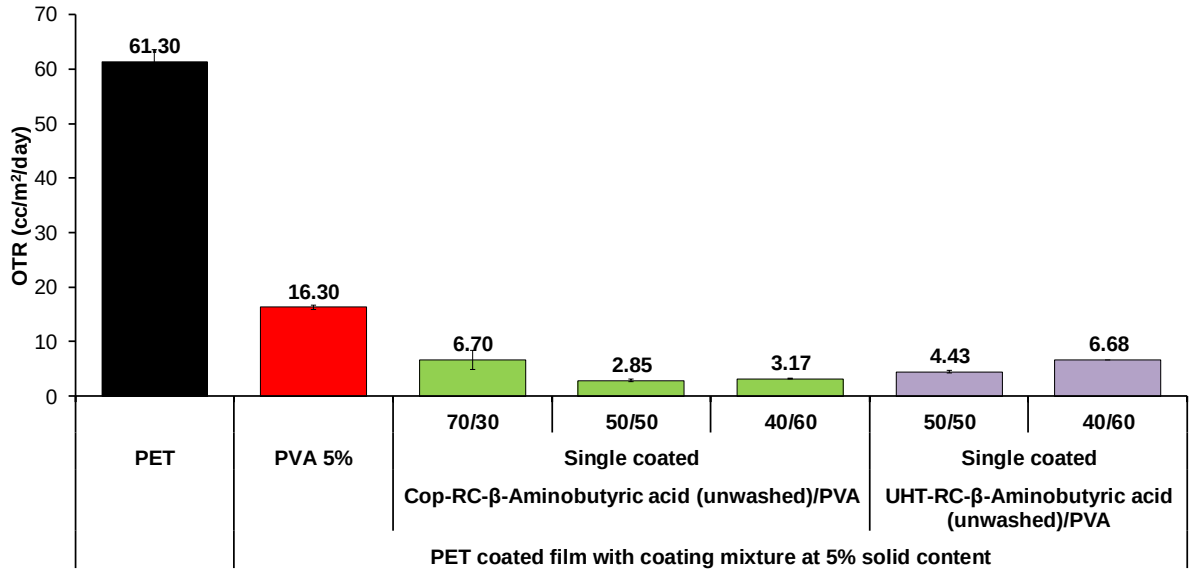


Fig. S19. OTR values of PET substrate (black), coated films with PVA (red) and coated films with various coating mixtures at different ratios of reconstructed LDH/PVA dispersions, Cop-RC-β-Aminobutyric acid/PVA/PET films (light green) and UHT-RC-β-Aminobutyric acid/PVA/PET films (light purple).

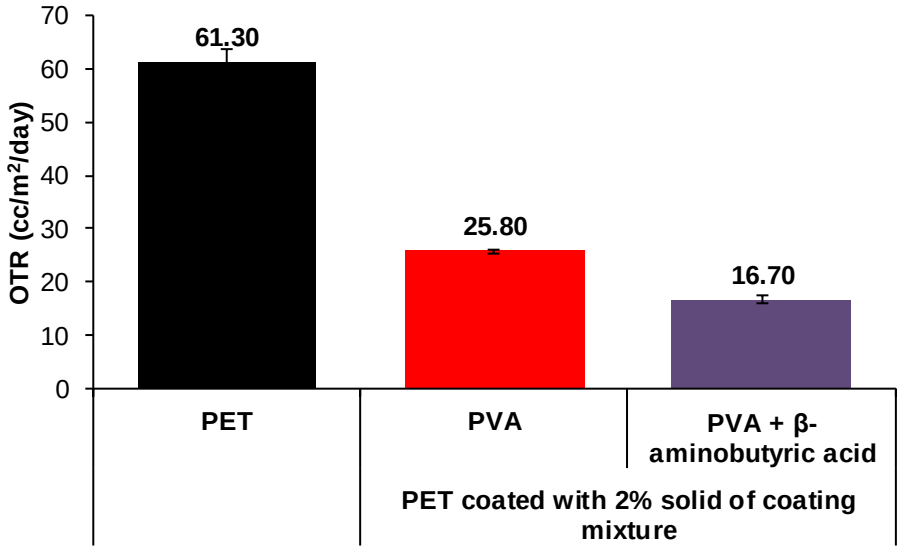


Fig. S20. OTR results of the coated films: Effect of amino acid on barrier property (without LDH).

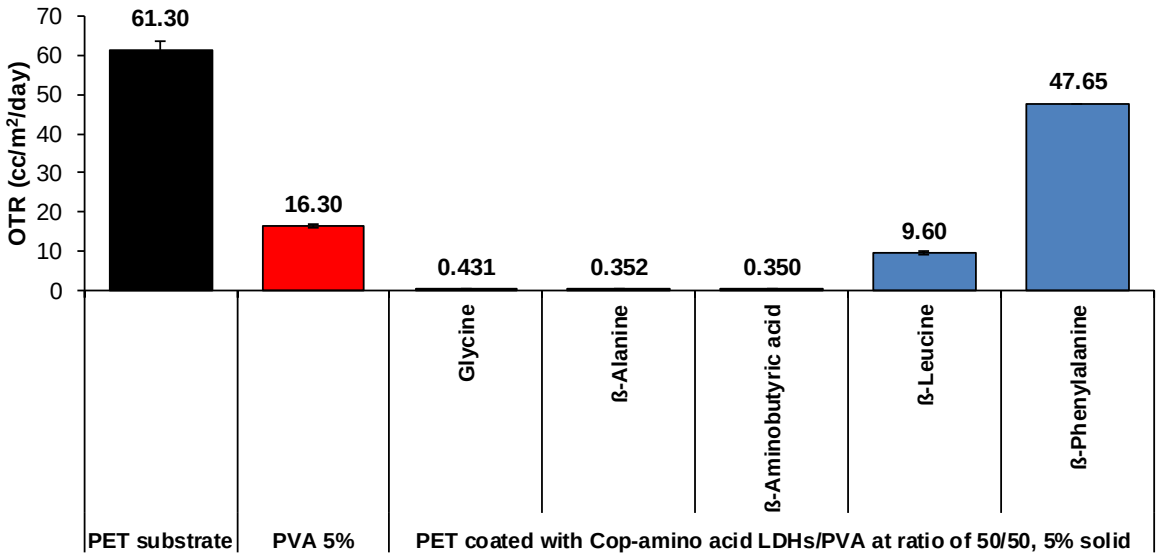


Fig. S21. OTR results of the coated films: comparison of Cop-RC-amino acids by recontruction using different non-polar amino acids on barrier property at LDH/PVA ratio of 50/50 at 5% solid content. The LDH used in the coating soluction was washed.

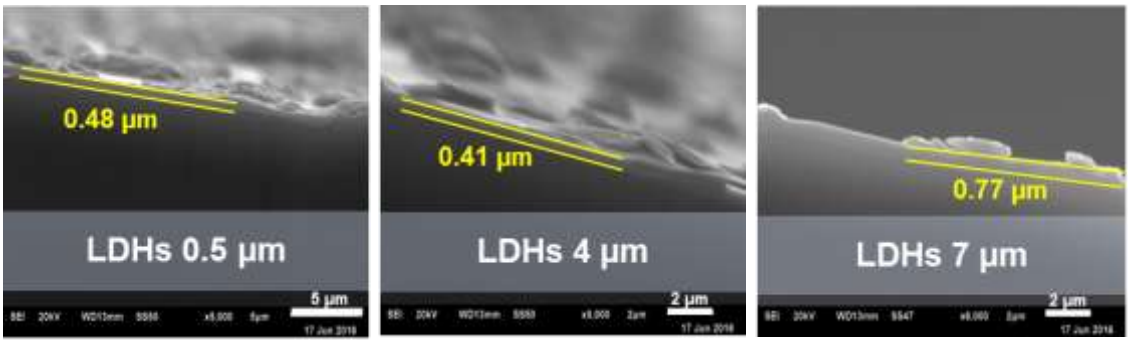


Fig. S22. Cross sectional SEM of coated films with the coatings with PVA/LDHs at 50/50 at 10% solid content.

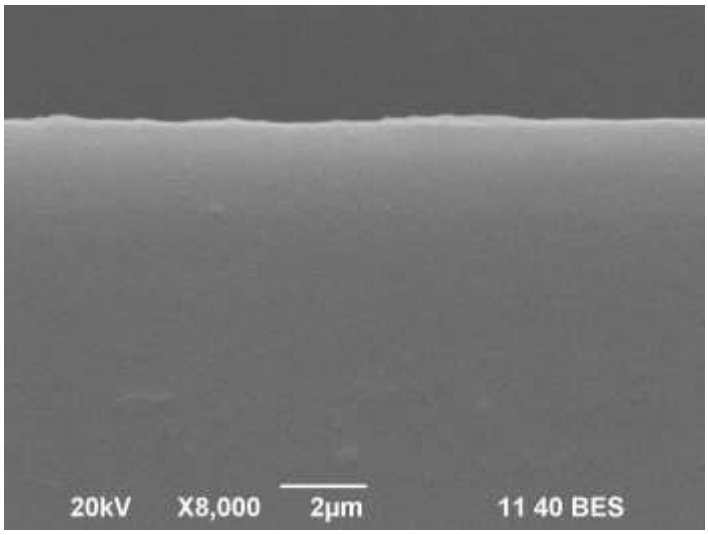


Fig. S23. Cross sectional SEM of coated films with the coatings with PVA/Cop-RC-β-amino butyric acid LDHs at 50/50 at 5% solid content.

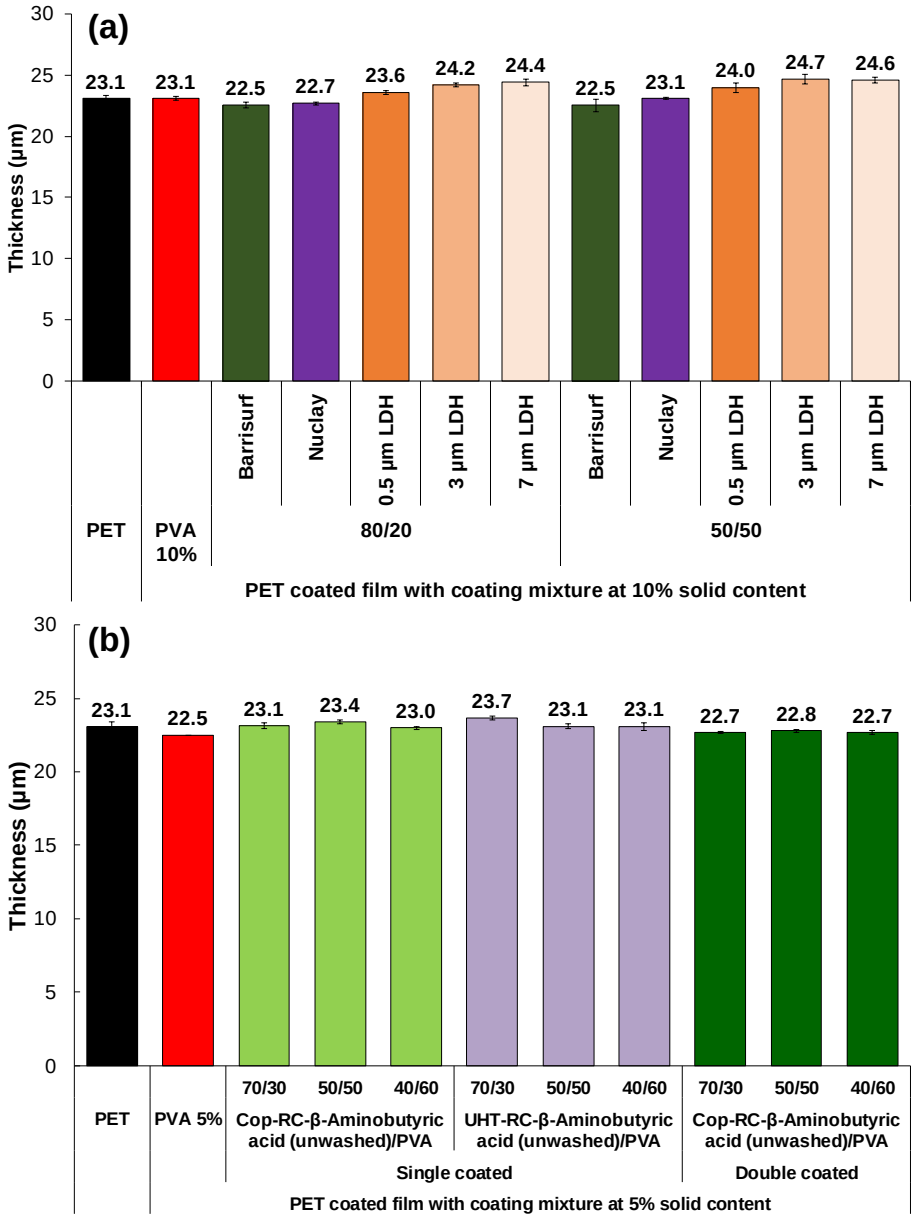


Fig. S24. Thickness of films (a) coated films with different LDHs and clays and (b) coated films with amino acid reconstructed LDHs.

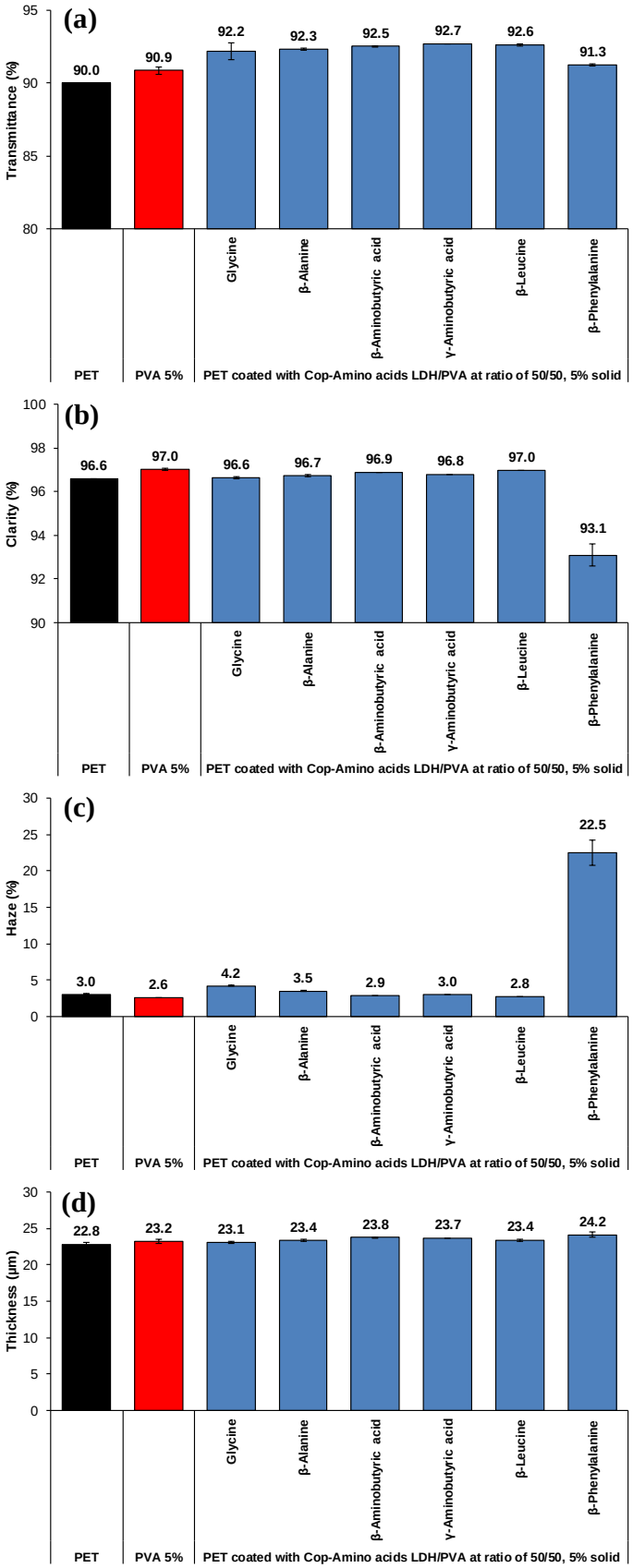


Fig. S25. Optical properties of coated films from Cop-RC amino acids by recontruction using different amino acids : (a) % transmission, (b) % clarity, (c) % haze and (d) film thickness.

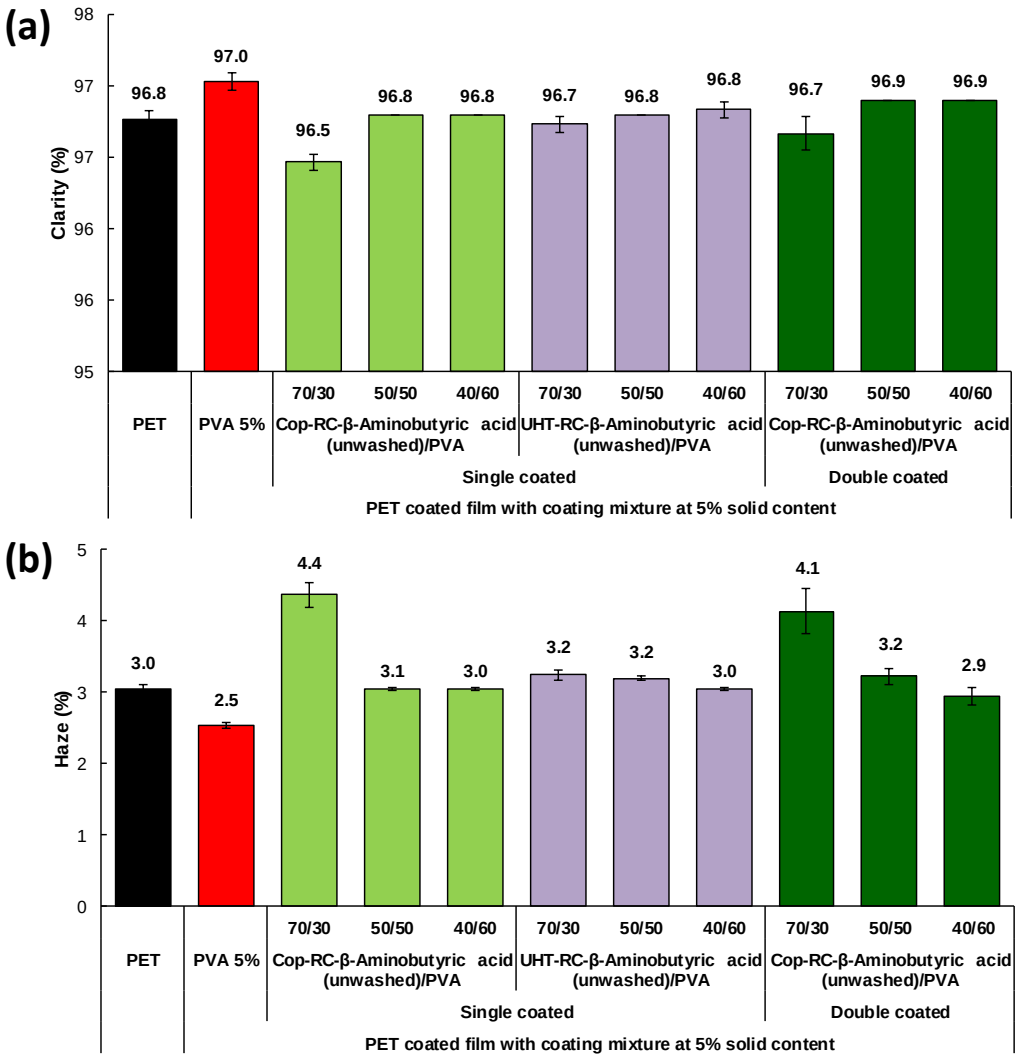


Fig. S26. Optical properties of Cop-RC-β-Aminobutyric acid/PVA/PET films with 5% solid content: (a) % clarity and (b) % haze.

Table S6. Oxygen permeability (OP) related to Fig. S21.[20]

		OTR ($cc\ m^{-2}\ day^{-1}$)	Thickness (μm)	OP ($cc\ mm\ m^{-2}\ day^{-1}$)
PET		61.3	22.8	1.398
PVA 5%		16.3	23.2	0.378
PET coated with Cop-Amino acids LDH/PVA at ratio of 50/50, 5% solid	Glycine	0.431	23.1	0.010
	β-alanine	0.352	23.4	0.008
	β-aminobutyric acid	0.350	23.8	0.008
	β-leucine	9.6	23.4	0.225
	β-phenylalanine	47.65	24.2	1.153

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