Macrocyclic oligomers as compatibilizing agent for hemp fibres/biodegradable polyester eco-composites

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Abstract: Ring:chain equilibria (RCE), existing under appropriate reaction conditions, between a linear polyester and the corresponding family of macrocyclic oligomers (MCOs), were exploited to develop an original compatibilizing pathway for preparing eco-composites based on hemp fibres and a biodegradable random co-polyester, namely poly(1,4-butylene adipate-co-terephthalate) (PBAT) with 50:50 adipate:therephthalate proportion. Cyclo-depolymerization (CDP) of PBAT was successfully carried out at high dilution using various solvents, catalysts, and reaction times. The reconversion of MCOs into linear chains by entropically-driven ring-opening polymerization (ED-ROP) occurs by simple heating in the bulk. This reaction, after optimization of catalyst amount, temperature, and reaction time, was used for the surface modification of hemp fibres. PBAT-based eco-composites containing hemp fibres as such or pre-modified by treatment with the MCOs were then prepared and characterized by morphological and mechanical analysis.

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Dear Editor,

I am sending the revised version of the manuscript POLYMER-18-340 *"Macrocyclic oligomers as compatibilizing agent for hemp fibres/biodegradable polyester eco-composites"* by L. Conzatti, E. Brunengo, R. Utzeri, M. Castellano, P. Hodge, and P. Stagnaro.

It has been revised according to the referees' comments: the whole text was improved whenever needed and the results obtained by thermogravimetric an dynamic-mechanical analysis of the eco-composites were added. All the revisions done are evidenced in red color.

We have answered all the remarks, as you can see in the attached "Response to Reviewers" file.

We warmly thank the referees for the suggestions aimed at improving the paper.

On behalf of all the authors, I warmly hope the paper can now deserve consideration for publication in **Polymer** journal.

Thank you in advance for your kind attention. Looking forward to hearing from you.

Sincerely yours,

Lucia Conzatti

Genova, May 11th, 2018

Ms. No. POLYMER-18-340

"Macrocyclic oligomers as compatibilizing agent for hemp fibres/biodegradable polyester eco-composites"

Response to Reviewers

Point-by-point the response to Reviewers is given in red in the following.

Reviewer #1 (Major Revision):

This work is very interesting in line with the current trends in biodegradable plastics and natural reinforcing fillers. The modification part is novel and the results are thoroughly presented.

We warmly appreciate the positive comments of the Reviewer on the work in the whole.

However, there some modification which will make this article much more useful to the readers.

1. Thermal properties of the composites may be added.

Experimental setup used thermogravimetric analysis (TGA) of the composites, results obtained from and related comments were added in the Manuscript at Pag. 7 – Lines 200-204, at Pag. 16 – Lines 372-379, and at Pag. 20-21 – Lines 464-476.

For homogeneity purposes, also TGA data under N_2 atmosphere of the fibres were reported in Table 3 of the revised Manuscript (Table 3, Pag. 17 – Lines 381-383).

2. The tensile strain decreased in the sample containing the MCO-modified fibres, how the explain effectiveness of the system to be at best at this composition as normally tensile strain is used to indicate the compatibility between matrix-filler.

To answer to this point, the following sentence was added at Pag. 21-22 – Lines 490-495:

"The slight decrease of the stress at break could be ascribed to a mechanical weakening of the hemp fibres due to the thermal treatment carried out during the ED-ROP reaction (190°C, 30 min). Even though a TGA isothermal analysis carried out at 200°C in O_2 atmosphere for 30 min revealed a good thermo-oxidative resistance of HF_{Na}s fibres (the weight loss is about 0.5%), the maintenance at high temperature in oxidative atmosphere could be slightly detrimental to the mechanical properties of the fibres, as reported by Prasad *et al.* [34]."

Moreover, in order to further support the enhanced fibre-PBAT adhesion/interaction due to the presence of MCOs, DMA tests were also carried out. Related data and comments were added in the revised Manuscript at Pag. 7 – Lines 208-210 and 217-223, and at Pag. 22 – Lines 496-515.

3. The composite at various compositions may be prepared and characterized for their mechanical properties.

The study of composites at various fibre composition is out of the scope of the present Manuscript, which is that of demonstrate the upcycling of HF residues on evaluating the efficiency of MCO as compatibilizing agent in PBAT-based eco-composites. For this purpose, such a high amount (about 40 wt.-%) of HF was added to the PBAT matrix.

The study of eco-composites with different amounts of fibres will be the object of a future work.

Reviewer #2 (Reject):

1.The reaction formula of MCO should be added.

The scheme of the ring:chain equilibrium of MCOs *vs.* PBAT was added (Scheme 2) in the text at Pag. 3 – Lines 85-86.

2.Why did the authors choose such a polyester with so wide PDI, about 8?

This polyester grade was suggested from BASF technical personnel as the most suitable for the preparation of eco-composites by melt blending technique.

3.In page 11, "the low melting range confirms the considerations on the relative volatility of the MCOs previously done". What's the relationship between the melting point and the volatility of MCOs? The DSC and TGA curves of MCOs are recommended to be added in the supporting information.

We agree with the referee: the relationship between the melting point and the volatility of MCOs is not directly proportional. However, DSC heating curve of MCOs shows a broad endothermic peak ranging from 30 to 60°C indicating a very low melting point. The relative volatility of MCOs could be enhanced in the conditions used for the removal of the *o*-DCB solvent, during which they were maintained at relatively high temperature (70°C) under vacuum. Moreover, it is to be outlined that the most volatile one is expected to be the monomeric cyclic n-butyl adipate.

A sentence was added at Pag. 9 – Lines 258-259 and that at Pag. 11 – Lines 288-289 was properly modified as "(this low melting range supports the considerations on the relative volatility of the MCOs previously done)".

Actually, DSC analyses were carried out, even though the related curves are not shown because they lack of significance in the Manuscript context. In facts, ED-ROP of MCOs takes place during the DSC (or TGA) heating run resulting in a dynamic system which leads to the PBAT formation.

4.In page 19, "HFNas, that only exhibits a feeble signal ascribable to carbonyl groups centred at 1735 cm-1." However, as shown in Figure 9, there is no peak at 1725 for the curve of HFNas, but there is a peak at around 1690.

The authors thank the referee for the suggestion, Figure 9 and relative caption (Pag. 18 – Lines 414-418) were improved inserting an inset to help the readers.

5.In page 22, although the storage modulus (E) of PBAT + HFNa-npMCOs is larger than that of PBAT + HFs, the stress at break (<sigma>b) and the elongation at break (<xi>) are lower obviously. Why?

To answer to this point, the following sentence was added at Pag. 21-22 – Lines 490-495:

"The slight decrease of the stress at break could be ascribed to a mechanical weakening of the hemp fibres due to the thermal treatment carried out during the ED-ROP reaction (190°C, 30 min). Even though a TGA isothermal analysis carried out at 200°C in O_2 atmosphere for 30 min revealed a good thermo-oxidative resistance of HF_{Na}s fibres (the weight loss is about 0.5%), the maintenance at high temperature in oxidative atmosphere could be slightly detrimental to the mechanical properties of the fibres, as reported by Prasad *et al.* [34]."

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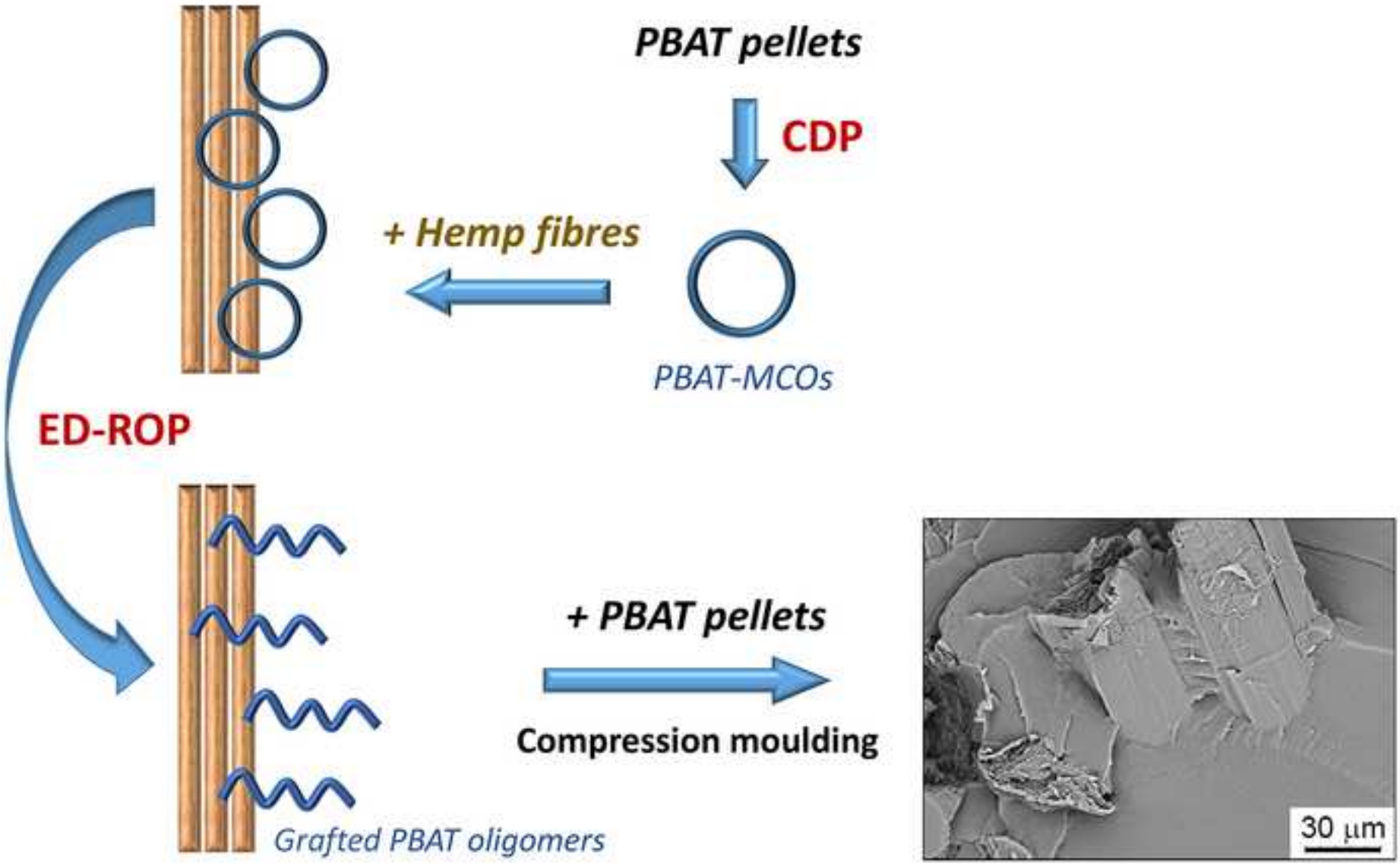
Graphical Abstract



Macrocyclic oligomers as compatibilizing agent for hemp fibres/biodegradable polyester eco-composites

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Abstract

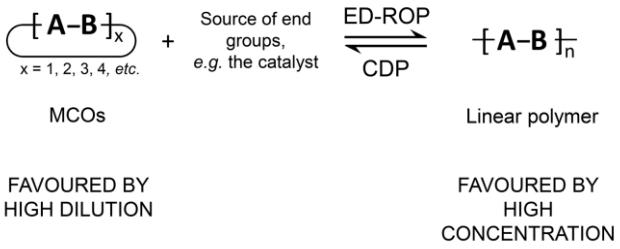
Ring:chain equilibria (RCE), existing under appropriate reaction conditions, between a linear polyester and the corresponding family of macrocyclic oligomers (MCOs), were exploited to develop an original compatibilizing pathway for preparing eco-composites based on hemp fibres and a biodegradable random co-polyester, namely poly(1,4-butylene adipate-*co*-terephthalate) (PBAT) with 50:50 adipate:therephthalate proportion.

Cyclo-depolymerization (CDP) of PBAT was successfully carried out at high dilution using various solvents, catalysts, and reaction times. The reconversion of MCOs into linear chains by entropically-driven ring-opening polymerization (ED-ROP) occurs by simple heating in the bulk. This reaction, after optimization of catalyst amount, temperature, and reaction time, was used for the surface modification of hemp fibres. PBAT-based eco-composites containing hemp fibres as such or pre-modified by treatment with the MCOs were then prepared and characterized by morphological and mechanical analysis.

Keywords: entropically-driven ring-opening polymerization (ED-ROP); macrocyclic oligomers (MCOs); hemp fibres; biodegradable polyester; eco-composites; mechanical properties.

1. Introduction

In the last decade, macrocyclic oligomers (MCOs) and their entropically-driven ring-opening polymerization (ED-ROP) have become of interest for the synthesis of polycondensation polymers such as polyesters, polycarbonates, certain polyamides, and various high-performance aromatic polymers [1-3]. ED-ROPs are based on ring:chain equilibria (RCE), *i.e.* the well-known equilibria existing, under appropriate reaction conditions, between a condensation polymer and the corresponding family of MCOs (Scheme 1) [1,2,4].



Scheme 1. A generalized ring:chain equilibrium. (1-column fitting image)

ED-ROP can be considered as a green process because to push the equilibrium towards the linear polymer generally no solvent is required, and, since the starting MCOs have no end groups and are strainless, no small molecules are released and little or no heat is evolved. Furthermore, high-molecular-weight polymers can be prepared in relatively short reaction times under atmospheric pressure, and the lower melt viscosity of the MCOs with respect to the polymer being formed allows easier processing by various techniques, such as pultrusion, resin-transfer moulding, reaction injection moulding, either concurrent with or just prior to polymerization [5-7]. ED-ROP has potential application in the preparation of composite materials [3], as voids due to the release of small volatile compounds are not created in the final products and the control of temperature throughout the reaction course is relatively facile.

In a wider context, growing global environmental and social concerns, high rate of depletion of petroleum resources, and new environmental regulations have encouraged the search for green processes, and in this respect, ED-ROP of strainless MCOs appears perfectly suited [1,2].

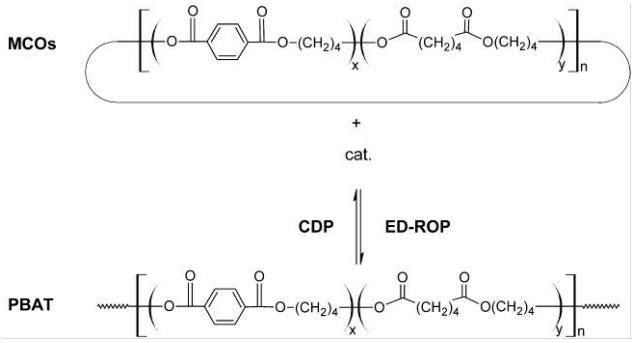
Furthermore, the interest for new materials derived from renewable sources as well as for recycle and valorization of low cost, waste or difficult-to-dispose natural products, such as wool or ligno-cellulosic fibres obtained from the stem of hemp, flax, jute, bamboo, etc. [8-12] is continuously increasing. In this field, many scientific research projects, as well as many commercial programs, are nowadays focused on eco-composites, *i.e.* composite materials, based on natural fibres embedded in natural or biodegradable polymer matrices [9,11], that can be easily degraded or bio-

assimilated, thus possessing environmental and ecological advantages over conventional composites. In particular, eco-composite materials containing ligno-cellulosic natural fibres (hemp, flax, jute, etc.) are characterized by low density, low environmental impact, recyclability and favourable cost/performance ratio [8,10,12].

Ligno-cellulosic fibres, which mainly consist of cellulose filaments embedded in a matrix of hemicellulose and lignin, have pronounced hydrophilic characteristics. This generally leads to a poor fibre-polymer interaction since the polymer matrix is typically apolar or only weakly polar. As a consequence, the attainment of eco-composites with good mechanical properties requires improvement in the compatibility between the two components [8,10,12,13].

Within this framework, in recent years we have started a study aimed at improving the adhesion between natural fibres (in particular wool) and various polymer matrices [14-17], exploring different compatibilization strategies.

In the present work the ED-ROP of the MCOs, obtained by cyclo-depolymerization (CDP) of a commercial biodegradable random co-polyester, namely poly(1,4-butylene adipate-*co*-terephthalate) (PBAT) (50:50 adipate:therephthalate), was exploited to develop a novel compatibilization pathway for achieving eco-composites based on PBAT and hemp fibres (HFs). As a matter of fact, the MCOs, previously adsorbed onto the hemp fibres and converted into oligomeric chains by ED-ROP (Scheme 2), can act as a compatibilizing agent capable, at least in principle, of interacting with both the fibre surface and the polyester matrix directly during melt mixing and/or by proper thermal treatments.



Scheme 2. Ring:chain equilibrium of PBAT. (1-column fitting image)

To this purpose, CDP of PBAT polyester was investigated at high dilution by varying the solvent, the catalyst and/or the reaction time. Selected MCOs were then used to optimize the conditions of the ED-ROP and then pre-adsorbed onto HFs previously mildly treated with aqueous NaOH. Once the ED-ROP of the MCOs adsorbed onto HFs has taken place, the uncut fibres were combed and incorporated into the PBAT matrix by compression moulding. The ensuing eco-composites were

then morphologically characterized to evaluate the fibre-matrix interaction and subjected to preliminary uniaxial tensile tests to investigate their mechanical properties.

2. Materials and methods

2.1. Materials

A commercial biodegradable, statistical poly(1,4-butylene adipate-*co*-terephthalate) (PBAT) grade (Ecoflex® F Blend A1200), kindly supplied by BASF (Germany), was used as the polyester matrix. $\overline{M}_n$ = 11.7 · 10^3 g/mol and $\overline{M}_w$ = 84.4 · 10^3 g/mol were evaluated by size exclusion chromatography (SEC). Values of T_g = -33°C, T_m = 118°C, ΔH_m = 26 J/g, T_c = 30°C and ΔH_c = 24 J/g were determined by differential scanning calorimetry (DSC). See the paragraph 2.6 for details on experimental conditions. The proportion of adipate versus terephthalate units was about 1:1, as determined by ^{1}H NMR analysis.

Raw hemp fibres of *Carmagnola* type, from which shives had been previously removed, were kindly supplied by Assocanapa (Italy) and used as received (HFs) or mildly treated ($HF_{Na}s$) in an aqueous solution of NaOH (0.2% wt./v) at 20°C for 48 h, following a procedure analogous to that reported in the literature [18].

Except where indicated otherwise, chemicals were purchased from Sigma-Aldrich and used as received.

2.2. Preparation of the MCOs

MCOs were obtained from PBAT by CDP at high dilution (1% wt./v), at solvent reflux temperature and in the presence of 3 mol% of a transesterification catalyst (namely *n*-dibutyltin(IV) oxide, *n*-Bu_2SnO, or titanium(IV) 2-ethylhexyloxide, $Ti(OR)_4$), by adapting a procedure already described for other polyesters [3,7]. *o*-Dichlorobenzene (DCB) or $CHCl_3$ were used as the solvent. The work up adopted for CDPs in DCB involved the solvent removal by rotoevaporation at 70°C and 2-3 mmHg followed by drying in a vacuum oven to constant weight. In the case of $CHCl_3$, the CDP products were recovered by solvent evaporation at room temperature in a fume hood, followed by careful drying under mild conditions. The CDP yield was determined as weight percentage with respect to the initial amount of PBAT. Reaction times were varied from 3 to 5 days.

The MCOs obtained from the CDP carried out under optimized conditions were used as such (that is non-purified: these are labelled npMCOs in the following where appropriate) or were purified by dissolution in the minimum amount of $CHCl_3$ and elution with CH_2Cl_2/acetone 94/6 v/v through a column of activated basic Al_2O_3 (150 mesh). Effective purification was checked by thin layer

chromatography (TLC), elemental analysis and SEC. Purified MCOs were labelled pMCOs in the following where appropriate.

Before use MCOs were stored under vacuum in anhydrous conditions.

2.3. ED-ROP of MCOs

ED-ROPs were carried out on the MCOs in isothermal conditions in a DSC pan. Samples (about 10 mg) were rapidly heated up to the selected temperature. The amount of *n*-Bu_2SnO catalyst (0-3 mol% with respect to the MCOs), reaction time (8-120 min) and temperature (180-200°C) were varied. The products obtained from the ED-ROPs were then characterized by SEC and DSC and compared with the commercial PBAT.

2.4. Modification of hemp fibres with the MCOs

On alkali treated HF_{Na}s two modification procedures were performed as follows: (i) npMCOs were pre-adsorbed onto HF_{Na}s (HF_{Na}-npMCOs) by immersing the fibres in a $CHCl_3$ solution (5% wt./v) of npMCOs; or (ii) *n*-Bu_2SnO was previously adsorbed onto HF_{Na}s through immersion of the fibres in a $CHCl_3$ solution (0.18% wt./v) of the catalyst and, after $CHCl_3$ evaporation, pMCOs were added as described for (i), obtaining fibres labelled HF_{Na}-C-pMCOs.

After $CHCl_3$ evaporation, the MCOs pre-adsorbed on the fibres underwent ED-ROP by simple heating in a P200E semi-automatic hot-plate press (Collin GmbH). For HF_{Na}-npMCOs ED-ROPs were carried out at 190 or 200°C for 30 or 120 min, while 190°C and 30 min were the conditions adopted for HF_{Na}-C-pMCOs. The so obtained fibres were then washed several times with $CHCl_3$ to remove ungrafted oligoester chains until TLC of the extracts did not reveal any trace of unreacted or ungrafted products. Extracts were analyzed by Fourier transform infrared spectroscopy (FTIR) and SEC.

A higher amount of HF_{Na}-npMCO fibres was obtained by fixing uncut, combed and slightly stretched HF_{Na} fibres to a frame and immersing them in a $CHCl_3$ solution (2.5% wt./v) of npMCOs (30 wt.% MCOs *vs.* fibres). After solvent evaporation at room temperature and pressure, ED-ROP of the pre-adsorbed npMCOs was performed at 190°C for 30 min. The ensuing HF_{Na}-npMCO fibres were carefully washed with $CHCl_3$ and dried at 60°C in a ventilated oven.

2.5. Preparation of hemp fibre/PBAT composites

Preliminary PBAT-based composites containing low amounts (less than 5 wt.%) of HF, HF_{Na}, HF_{Na}-C-pMCO, or HF_{Na}-npMCO fibres were prepared by placing slightly stretched fibres between

two 0.3 mm thick sheets of PBAT and by moulding the resulting "sandwich" in the semi-automatic press at 180 °C, *i.e.* above T_m, for 1 min at 5 bar and then 4 min at 160 bar.

PBAT-based composites (10x10x0.1 cm sheets) containing higher amounts (about 40 wt.%) of uncut oriented HF, HF_{Na}, and HF_{Na}-npMCO fibres were then prepared by compression moulding through a two-step method: (i) impregnation of combed and slightly stretched fibres into melted PBAT (180°C, 8 min) and achievement of sheets by moulding at 180°C, 1 MPa, 7 min; (ii) moulding (150°C, 1 MPa, 3 min) two so-obtained sheets with fibres oriented in the same direction.

2.6. Characterizations

SEC analyses were carried out using a Perkin Elmer chromatography system with a Diode Array Detector 235C and operating at a flow rate of 1 mL/min. $CHCl_3$ was used both as solvent and eluent. Column set: 10^3 (PL GEL, 30 cm, 5 μm), 500 Å (PL GEL, 30 cm, 5 μm), 500 Å (PL GEL, 30 cm, 10 μm), 100 Å (Styragel HR1, 30 cm, 5 μm). PBAT pellets were analysed with the following column set: 10^5 (Styragel HR5, 30 cm, 5 μm), 10^4, 10^3, 500 Å (PL GEL, 30 cm, 5 μm).

TLC analysis was carried out by using CH_2Cl_2/acetone 94/6 v/v as eluent.

Elemental analysis was carried out by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Fisons Instruments Horizon instrument to evaluate Sn content in selected MCOs samples.

Room temperature ^1H NMR spectrum of PBAT dissolved in deuterochloroform ($CDCl_3$) was obtained with a Bruker Avance-500 spectrometer (no internal chemical shift reference).

FTIR spectroscopic characterization of PBAT, MCOs, fibres, and extracts from the fibre washing was performed with a Perkin Elmer Spectrum Two™ FTIR spectrometer operating in the attenuated total reflectance (ATR) mode and recording absorbance spectra in the wave number range 4000-400 cm^{-1}.

Room temperature wide angle X-ray diffraction (WAXD) spectra of hemp fibres were obtained using a Siemens diffractometer model D-500 equipped with a Siemens FK 60-10 2000W tube (Cu K_α radiation, λ = 0.154 nm). The operating voltage and current were 40 kV and 40 mA, respectively. Data were collected from 5 to 40° 2θ at 0.02° 2θ intervals. The percentage crystallinity index (*CI*) of cellulose in hemp fibres was determined by extracting the three crystalline peaks between 10 and 30° 2θ from the diffraction intensity profiles with a non-linear curve-fitting process [19,20]. A peak fitting commercial software (OriginPro 2015, OriginLab Co.) was used, assuming for each peak Lorentzian functions. The *CI* was calculated from the ratio of the area of the crystalline peaks to the total area.

A Mettler DSC 821^e calorimeter was used for thermal characterization of the materials and for performing small-scale ED-ROPs in the DSC pan. For characterization of the products obtained from CDPs a single heating run between 0 and 200°C (scan rate 20°C/min) was performed. Heating-cooling-heating cycles from 0 up to 200°C (scan rate 20°C/min) were applied for PBAT pellets and products obtained from ED-ROPs.

Thermogravimetric analysis (TGA) measurements were performed with a PerkinElmer TGA7 analyzer operating in dynamic mode. Samples of PBAT and fibres of about 10 mg were heated at 20 °C/min under O_2 from 50 to 900°C (gas flow rate 40 mL/min). The water content (mass loss at 150°C), the decomposition temperatures corresponding to 5 wt.% mass loss (T_5) and the maximum rate of decomposition (T_{Vmax}) were determined. Samples of composites of about 10 mg were heated at 10 °C/min under N_2 from 30 to 750°C (gas flow rate 40 mL/min) for the evaluation of the fibre content. The onset (T_{onset}) and the T_{Vmax} degradation temperatures were determined. For reference purpose, neat PBAT and all HFs were analysed in the same experimental conditions.

Morphological analysis was carried out by scanning electron microscopy (SEM) using a Hitachi TM3000 benchtop SEM microscope operating at 15 kV acceleration voltage. Fibres and fragile surfaces of composites fractured in liquid N_2 were sputtered with gold using a Quorum Q150R ES sputter coater (2M Strumenti) at 20 mA for 5 min prior to the observation. Moreover, a FE-SEM Zeiss Supra 40VP was used for a deeper morphological analysis of the samples after dynamic-mechanical analysis (DMA).

Uniaxial tensile tests were performed by using a displacement-controlled dynamometer (Instron 5565) according to the ASTM D412 TC standard method (25°C, load cell 5 kN, constant crosshead speed 20 mm min^{-1}) on rectangular specimens (80x10x1 mm). Tensile modulus (E), stress (σ_b) and strain (ε_b) at break were evaluated for neat PBAT matrix and its composites with hemp fibres. Mechanical parameters were measured on more than 6 specimens and the average values were calculated.

Dynamic-mechanical measurements were carried out on rectangular specimens (40x10x1 mm) with a strain-controlled rotational rheometer MCR301 (Anton Paar). The range of viscoelastic linearity was determined through amplitude sweep tests performed at 1 Hz and 25°C in the strain range 0.01÷100%; room temperature frequency sweep tests were then carried out in the torsion mode at 0.1% amplitude deformation in the frequency range 0.1÷50 Hz, both in longitudinal and transversal direction (*i.e.*, with fibres parallel or perpendicular to the clamp axis, respectively). Elastic (G') and dissipative (G") components of the modulus were determined.

3. Results and Discussion

3.1. CDP of PBAT

CDPs of PBAT were carried out by using different solvents (DCB or $CHCl_3$), catalysts ($Ti(OR)_4$, with R = 2-ethylhexyl, or *n*-Bu_2SnO) and/or reaction times (3-5 days), as described in the Materials and methods section and summarized in Table 1.

Table 1. CDPs of PBAT carried out at high dilution (1 %wt./v) and SEC characterization.

Run	Solvent	Catalyst	Reaction time (days)	Product Yield[a] (wt.%)	Fraction with Mp < 4000[a] (%)
1	DCB	$Ti(OR)_4$[b]	3	88	16
2	DCB	$Ti(OR)_4$[b]	4	71	33
3	DCB	*n*-Bu_2SnO	3	25	85
4	$CHCl_3$	*n*-Bu_2SnO	5	100	100
5	$CHCl_3$	*n*-Bu_2SnO	4	100	100
6	$CHCl_3$	*n*-Bu_2SnO	3	100	100

[a] Calculated as weight percentage of recovered reaction products with respect to the initial amount of PBAT.

[b] Obtained from SEC analysis.

[c] R: 2-ethylhexyl.

The reaction was conveniently monitored by SEC analysis. SEC traces of the starting PBAT pellets and of the equilibrated CDP mixtures obtained under selected experimental conditions are compared in Fig. 1. Depending on reaction conditions, the SEC traces present either a major peak of relatively high molecular weight (Run 1 and 2) or a series of peaks of low molecular weight (Run 6). In the former case, CDP of PBAT does not occur to an appreciable extent and PBAT is practically recovered unaltered; in the latter reactions the MCOs are successfully formed, as evidenced by the series of peaks corresponding to MCOs of different ring sizes and, possibly, compositions (since PBAT is a copolyester with aliphatic-aliphatic and aliphatic-aromatic ester linkages having non-identical chemical reactivity). The relative amount of each species present in the reaction product was calculated from the SEC traces as percentage area.

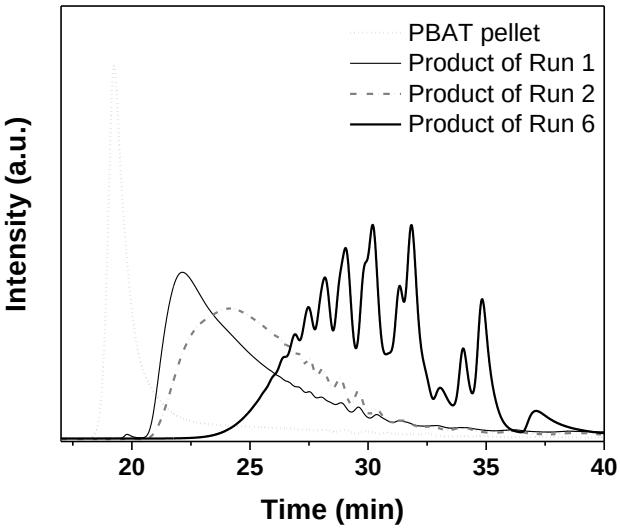


Fig. 1. SEC traces of PBAT and some selected products obtained from its CDP. (1-column fitting image)

No significant amounts of low molecular weight species were obtained with the Ti-based catalyst (Run 1 and 2), but MCOs were successfully prepared by CDP in both solvents when *n*-Bu_2SnO was the catalyst. However, when DCB was used as the solvent (Run 3) the work-up following the reaction led to the recovery of a very low amount of MCOs product (25%). This is ascribable to the loss of lower molecular weight fraction of MCOs, considering that the monomeric cyclic *n*-butyl adipate is expected to be the most volatile one.

By using $CHCl_3$ as solvent, which has a much lower boiling point than DCB, the work-up was easier, as indicated in the Materials and methods section, and quantitative yields in MCOs were obtained (Run 4-6). The effect of the reaction time was also evaluated carrying out the CDP with the $CHCl_3$/*n*-Bu_2SnO pair: as evidenced in Table 1 and in Fig. 2, 3 days at reflux temperature are necessary for obtaining the MCOs in high yield (Run 6).

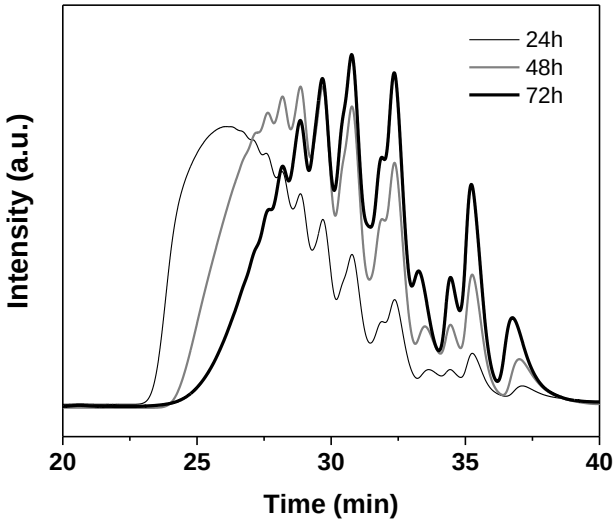


Fig. 2. SEC traces of products obtained from CDP of PBAT carried out at different reaction times (see Table 1, Runs 4-6). (1-column fitting image)

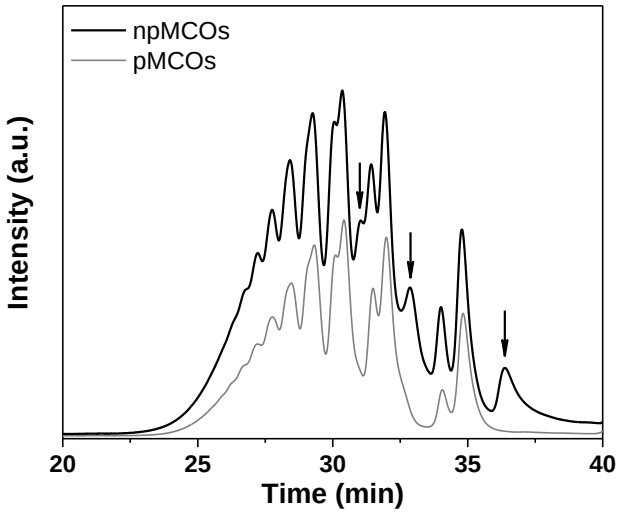


Fig. 3. SEC traces of the MCOs obtained as in Run 6 of Table 1, before and after purification. (1-column fitting image)

Accordingly, the MCOs obtained from Run 6 were selected to perform successive ED-ROP experiments and HF modification. The MCOs were used either as directly obtained from the CDP (npMCOs), or were purified by adsorptive filtration on Al_2O_3 (pMCOs) [7] to remove as much as possible any residue of transesterification catalyst and possible traces of linear oligomeric species. A yield of 65 wt.% was found after filtration. TLC carried out on the MCOs before and after purification indicated the removal of the most polar species. Furthermore, in the SEC traces of purified MCOs the peaks at 240, 480 and 750 g/mol, probably ascribable to linear oligomeric species [21], disappeared (Fig. 3 and Table 2). The presence of the tin-based catalyst used for the

CDP was checked by elemental analysis for Sn both in npMCOs and pMCOs. A content of 1.44 wt.% of Sn (that corresponds to the 3 mol% catalyst introduced) was found in npMCOs, which were isolated without any washing after CDP; whereas after the filtration on Al_2O_3 practically all the catalyst was removed from pMCOs, since only traces (< 0.1%) of tin were detected.

DSC analysis showed a similar thermal behaviour for the MCOs both before and after purification. Thus, a broad endothermic peak centred at about 50°C is observed upon heating (this low melting range supports the considerations on the relative volatility of the MCOs previously done).

Table 2. SEC Characterization of the MCOs before and after purification.

npMCOs		**pMCOs**	
M_p[a] **(g/mol)**	**Area (%)**	M_p[a] **(g/mol)**	**Area (%)**
3930	9.7	3950	9.4
2420	4.8	2410	4.3
2020	6.5	2000	7.8
1630	9.3	1600	11.1
1250	12.4	1230	15.2
990	6.3	980	6.7
910	9.0	900	14.1
750	3.9	-	-
680	6.5	680	6.8
600	10.2	600	14.3
480	6.1	-	-
370	3.5	370	2.3
320	7.0	320	8.1
240	4.8	-	-

[a] Molecular weight at peak.

3.2. ED-ROP of the MCOs

Several ED-ROP runs on the MCOs were carried out under N_2 in a pan placed in the DSC furnace with the aim of investigating the influence of *n*-Bu_2SnO concentration, reaction time and temperature on molecular and thermal characteristics of the ensuing polyesters. For this purpose, samples of the MCOs containing different amounts of *n*-Bu_2SnO catalyst were obtained by mixing solutions (using $CHCl_3$ as a solvent) of npMCOs, which were assumed to contain unvaried (with respect to the amount introduced for the CDP) *n*-Bu_2SnO content (3 mol%), and of pMCOs (assumed to be completely free of catalyst). As shown by SEC traces of Fig. 4, the presence of *n*-

Bu_2SnO is necessary for efficient ED-ROPs of MCOs in the selected conditions. Products with higher molecular weights were obtained by increasing the amount of *n*-Bu_2SnO.

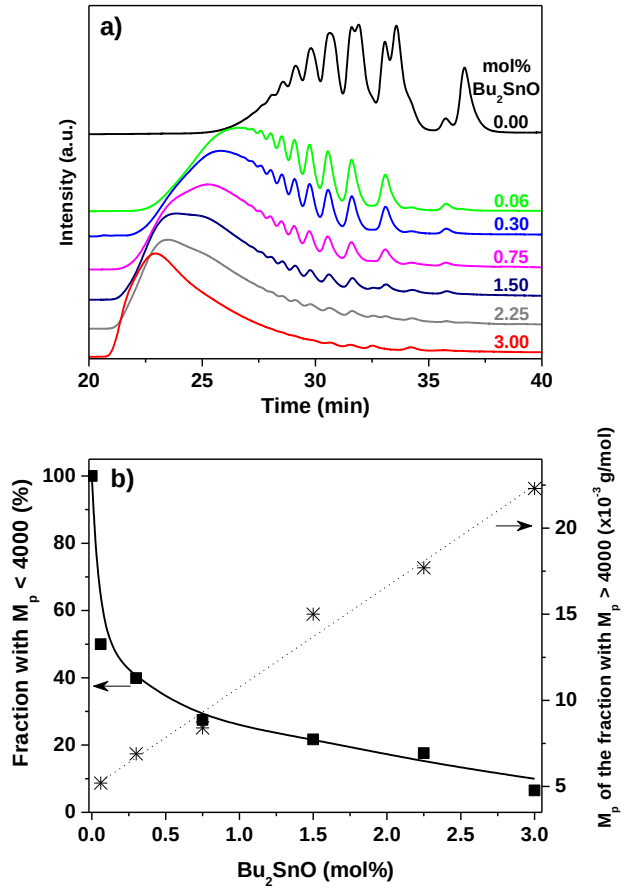


Fig. 4. SEC traces of products obtained from ED-ROPs of the MCOs (180°C, 120 min) carried out by varying the amount of *n*-Bu_2SnO (a); Plots of M_p and Fraction with M_p < 4000 *vs.* *n*-Bu_2SnO amount (b). (1-column fitting image)

Thus ED-ROP runs were carried out on npMCOs (that is containing 3 mol% *n*-Bu_2SnO) varying the reaction time. Data obtained from SEC analysis of ED-ROP products shown in Fig. 5 indicate that ED-ROP of npMCOs takes place to a certain extent already after 8 min and the molecular weight of ED-ROP products being formed increased rapidly in the first 30 min in the DSC pan. Reaction times longer than 30 min did not lead to substantial further increase of the molecular weight of the products.

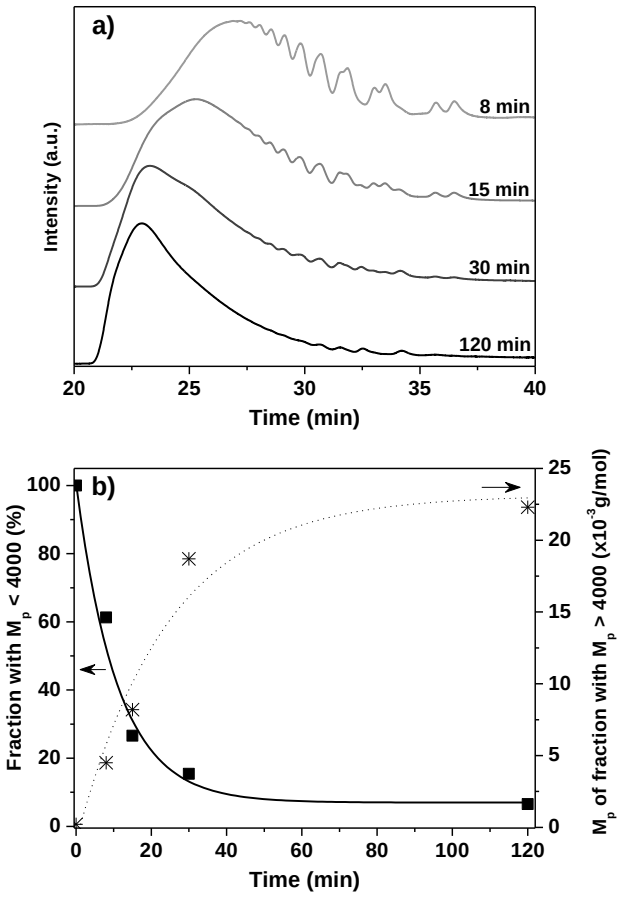


Fig. 5. SEC traces of products obtained from ED-ROPs of the MCOs (3 mol% *n*-Bu_2SnO, 180°C) carried out by varying the reaction time (a); Plots of M_p and Fraction with M_p < 4000 *vs.* reaction time (b). (1-column fitting image)

ED-ROP runs were finally carried out on npMCOs fixing reaction time at 30 min and varying the temperature (180, 190, 200°C). Obtained SEC data (not shown here) indicate that for temperatures higher than 190°C the molecular weight reaches a plateau value of about 21000 g/mol and the amount of low molecular species is lower than 10%.

DSC analysis of the ED-ROP products (data not shown) confirmed the results obtained from SEC analysis. The product obtained from ED-ROP of npMCOs carried out at 190°C for 30 min presents a thermal behaviour similar to that of the original PBAT pellets (melting temperature about 120°C).

3.3. Surface modifications of hemp fibres

Raw hemp fibres, previously freed of shives as indicated in the Materials and methods section, were considered for the preparation of eco-composites based on Ecoflex®, a commercial grade of the biodegradable PBAT copolyester. In order to improve their compatibility with the polymer matrix, the fibres were firstly treated under mild conditions with an aqueous solution of NaOH to make

their functional groups more accessible for successive reactions. Natural cellulosic fibres are complex assemblies including cellulose, hemicellulose, lignin, pectin, waxes and water-soluble substances [22]. The removal of the non-cellulosic materials from the fibre surface is beneficial for interaction with polymer matrices and propaedeutic for the successive chemical modification. Among the proposed methods, alkali treatment is widely used for removing non-cellulosic components and part of the amorphous cellulose [23,24]. However, this treatment can significantly modify the crystalline structure of the fibres. The mild conditions adopted in this work for treating HFs [18], resulted in better separated fibres with cleaner surface topography (Fig. 6 a,b) due to a partial removal of non-cellulosic components.

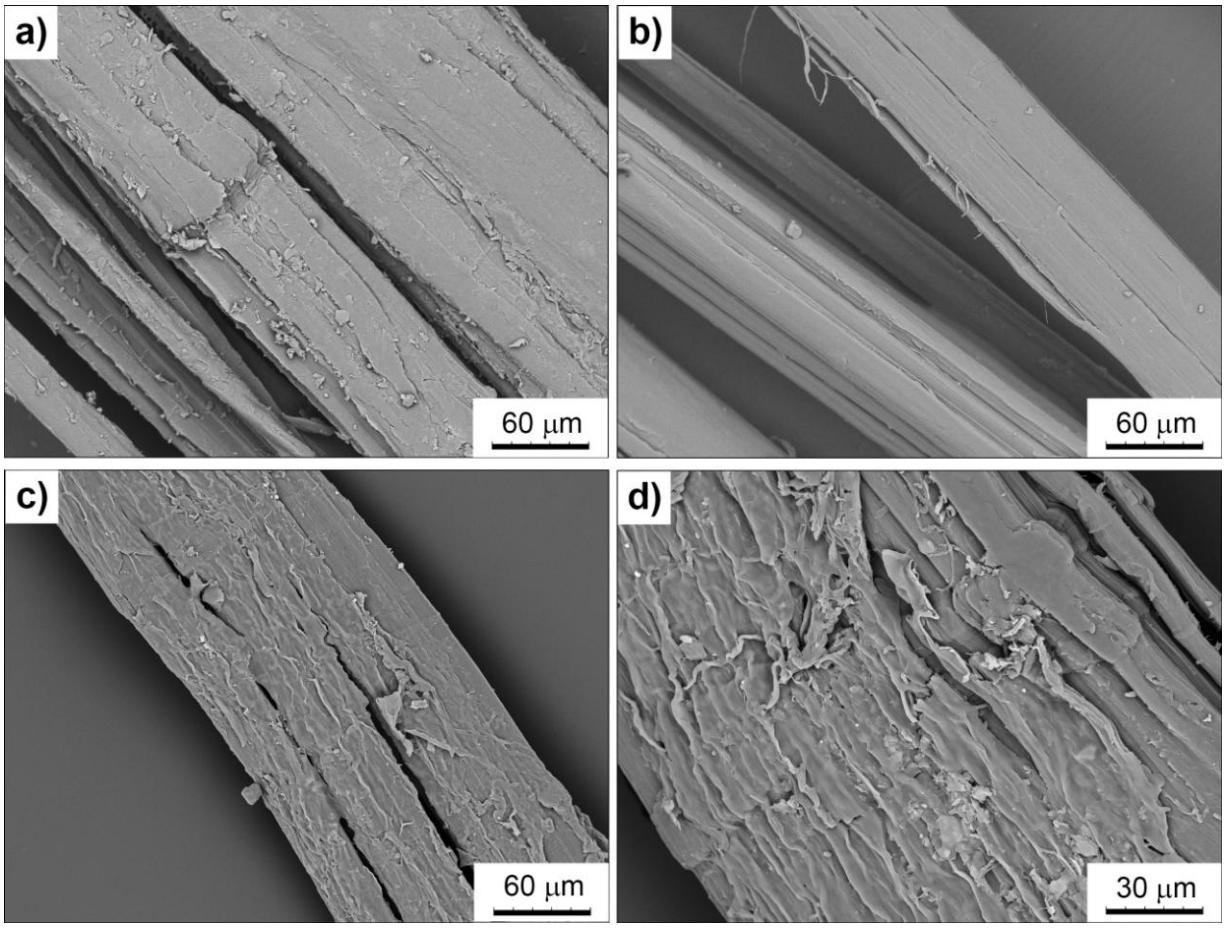


Fig. 6. SEM micrographs of: (a) HFs, (b) HF_{Na}s, and (c,d) HF_{Na}-npMCOs. (2-column fitting image)

ATR-FTIR analysis of HF and HF_{Na} fibres confirmed SEM observations indicating the removal of hemicellulose component as a consequence of the NaOH treatment. In particular, as shown in Fig. 7, the intensity of the peak at 1735 cm^{-1}, characteristic of the C=O stretching vibration of carboxyl and acetyl moieties in hemicelluloses (xyloglucan) [25], decreases as well as that of the peak at 1243 cm^{-1}, which corresponds to the C-O linkage, as found in guaiacyl aromatic methoxyl and acetyl moieties of xyloglucan [25]. On the other hand, the peaks at 2920 and 2850 cm^{-1} corresponding to the C-H stretching of lignin and cellulose [26,27] become more evident.

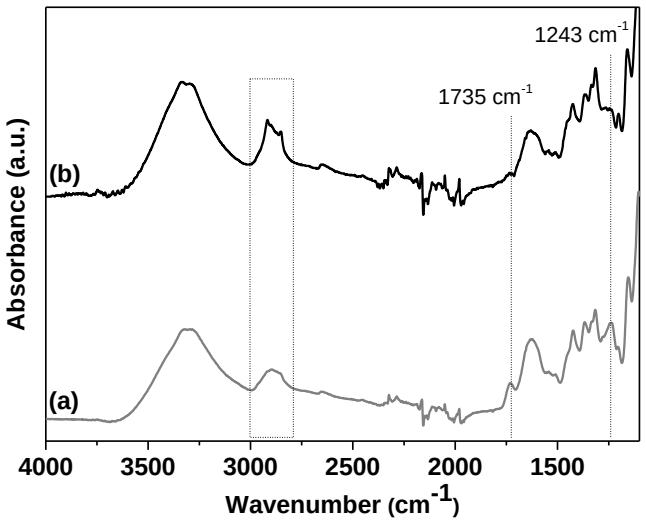


Fig. 7. ATR-FTIR spectra of: (a) HF, and (b) HF_{Na} fibres. (1-column fitting image)

No great differences in the crystalline structure as well as in the crystallinity index (*CI*) were found before and after the mild alkali treatment of hemp fibres used here. Indeed, both diffractograms (Fig. 8) show the four XRD reflections typical of cellulose I at 15, 16.4, 22.6, and 34.3° 2θ corresponding, respectively, to (101), (10-1), (002), and (040) crystallographic planes [28,29].

By peak deconvolution a *CI* value of 85% was calculated for HFs and of 87% for HF_{Na}s, that is a slightly higher value, also considering the experimental error intrinsic to the technique. However, it is worth mentioning that the fibre crystallinity index is generally used for comparison purpose before and after different treatments rather than to evaluate absolute crystallinity [30-32]. Moreover, the two peaks at 15 and 16.5° appeared partially overlapped, indicating that the HF_{Na} fibres still contain a certain amount of amorphous material [33], as expected following a mild alkali treatment as in the present case; when these two peaks are well separated and pronounced the fibres contain higher amounts of crystalline cellulose.

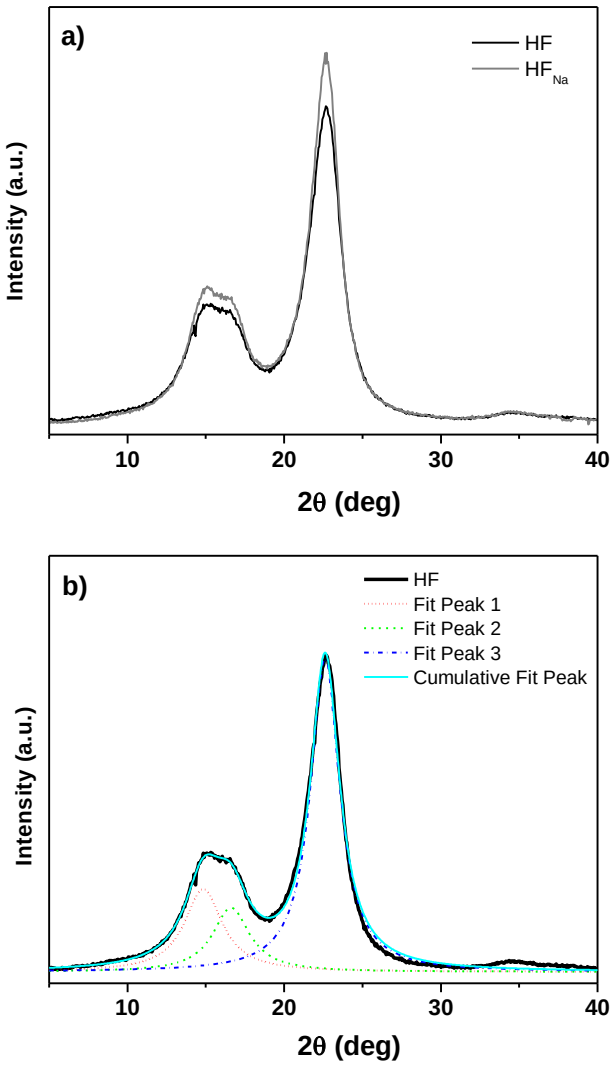


Fig. 8. XRD diffractograms of: (a) HF and HF_{Na} fibres, and (b) example of peak deconvolution of the XRD pattern of HFs. (1-column fitting image)

Thermal and thermo-oxidative stability of hemp fibres before and after the treatment with sodium hydroxide and the subsequent surface modification with the MCOs (see later in the text) were investigated by TGA analysis in dynamic mode. Relevant TGA data collected are summarized in Table 3. The fibre treatment with NaOH slightly increases the temperature at which the fibres start to degrade under O_2 atmosphere; indeed, T_5 values of HF_{Na}s is about 10 higher than that of HFs. This can be explained by the partial removal of non-cellulosic and amorphous cellulose components (which decompose at lower temperatures) with consequent slight increase in crystallinity. Both under O_2 and N_2 atmosphere, the T_{Vmax} values before and after NaOH treatment are quite similar.

Table 3. Water content at 150°C and T_5 and T_{Vmax} decomposition temperatures of hemp fibres determined by TGA.

Sample	H_2O content @ 150°C (wt.%)	Under O_2		Under N_2
		T_5 (°C)	T_{Vmax} (°C)	T_{Vmax} (°C)
HFs	2.2	307	358	374
HF_{Na}s	2.5	315	355	371
HF_{Na}-C-pMCOs	1.7	327	368	-
HF_{Na}-npMCOs	1.8	325	369	378

The surface modification of HF_{Na}s with the synthesized MCOs could in principle be accomplished through different procedures:

(i) adsorption of the MCOs onto HF_{Na}s followed by ED-ROP directly during mixing with PBAT in internal mixer;

(ii) adsorption of non-purified npMCOs, i.e. the crude MCOs as obtained from CDP still containing the transesterification catalyst, and their subsequent ED-ROP onto HF_{Na}s prior to incorporation of the so-modified fibres into the PBAT matrix;

(iii) previous anchorage of the transesterification catalyst onto HF_{Na}s, subsequent adsorption of purified pMCOs, that is cleaned by catalyst through elution on Al_2O_3, and ED-ROP prior to fibres incorporation in the PBAT matrix.

The easiest and fastest strategy (i) unfortunately gave composite materials with no appreciable improvement in their final properties [17]; this could be ascribed to uncontrolled ED-ROP conditions and too short residence times in the mixer. As a consequence, (ii) and (iii) compatibilization strategies appeared more promising and were further investigated.

As detailed in the Materials and methods section, two procedures for modification of HF_{Na}s with the MCOs, respectively starting from npMCOs or pMCOs macrocycles, were followed. The ED-ROP of the MCOs adsorbed onto the hemp fibres was performed by using the reaction conditions (190°C, 30 min) established by the polymerization experiments previously carried out in the DSC pan. The two MCO-modified fibre samples obtained after ED-ROP and extraction of unreacted or ungrafted products were called HF_{Na}-npMCOs and HF_{Na}-C-pMCOs, respectively.

The presence of PBAT oligomers (M_p ranging from 5000 to 7000 g/mol) in the soluble fractions obtained by washing both MCO-modified fibre samples with $CHCl_3$ was ascertained by FTIR and SEC analyses. This finding confirms that unreacted macrocycles and/or ungrafted linear oligomers were effectively removed from hemp fibres. As a consequence, the reacted portion which remains on the fibres is actually grafted. The ATR-FTIR analysis of fibres modified by both procedures (ii) and (iii) featured the presence on their surface of the PBAT moieties, as desired. In particular, the

peaks at 1715 and 1270 cm^{-1}, respectively due to the stretching modes of C=O and C-O of the ester linkages belonging to the polyester chains, were observed (Fig. 9). It is worth noticing that these peaks are absent in the spectrum of alkali treated HF_{Na}s, that only exhibits a feeble signal ascribable to carbonyl groups centred at 1735 cm^{-1}.

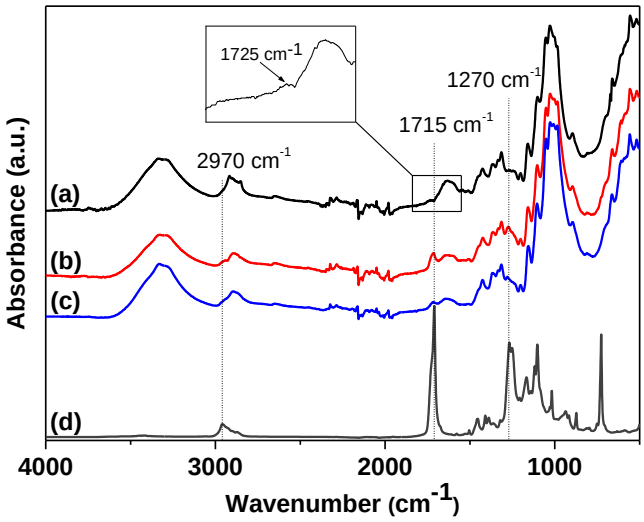


Fig. 9. ATR-FTIR spectra of: (a) HF_{Na}s, (b) HF_{Na}-npMCOs, (c) HF_{Na}-C-pMCOs, and (d) PBAT. Inset shows the ATR-FTIR spectrum of HF_{Na}s in the 1950-1550 cm^{-1} window. (1-column fitting image)

As shown by the parameters collected in Table 3, the surface modification of HF_{Na}s with the MCOs results in an improvement of the thermo-oxidative stability of the fibres. Moreover, the water content of fibres stored in an ambient environment (T ≈ 25 °C, RH ≈ 65%), evaluated as the weight loss at 150°C, decreases after modification with the MCOs, indicating, as expected, a reduction of the surface hydrophilicity.

SEM images of Fig. 6 c,d clearly show the presence of a polymeric layer covering the surface of fibres modified with npMCOs. The increase in thermo-oxidative stability of both samples of MCO-modified fibres can be ascribed to the protection exerted by this polymeric layer, being the thermo-oxidative decomposition temperatures T_5 and T_{Vmax} recorded for PBAT in the same conditions, respectively 344 and 415°C.

3.4. PBAT/hemp fibres eco-composites

In order to evaluate the effect of the fibre modification on the fibre-polymer adhesion, preliminary tests of adhesion were carried out on composites containing < 5 wt.% of HF, HF_{Na}, HF_{Na}-npMCO or HF_{Na}-C-pMCO fibres prepared by placing slightly stretched fibres between two sheets of PBAT

(previously obtained by compression moulding of PBAT pellets) and by moulding the resulting "sandwich" in the hot-press, as detailed in the Materials and methods section.

The ensuing samples were then fractured in liquid nitrogen and the morphological characterization of their fractured surfaces was performed by SEM. Some representative images taken at the same magnification were shown in Fig. 10.

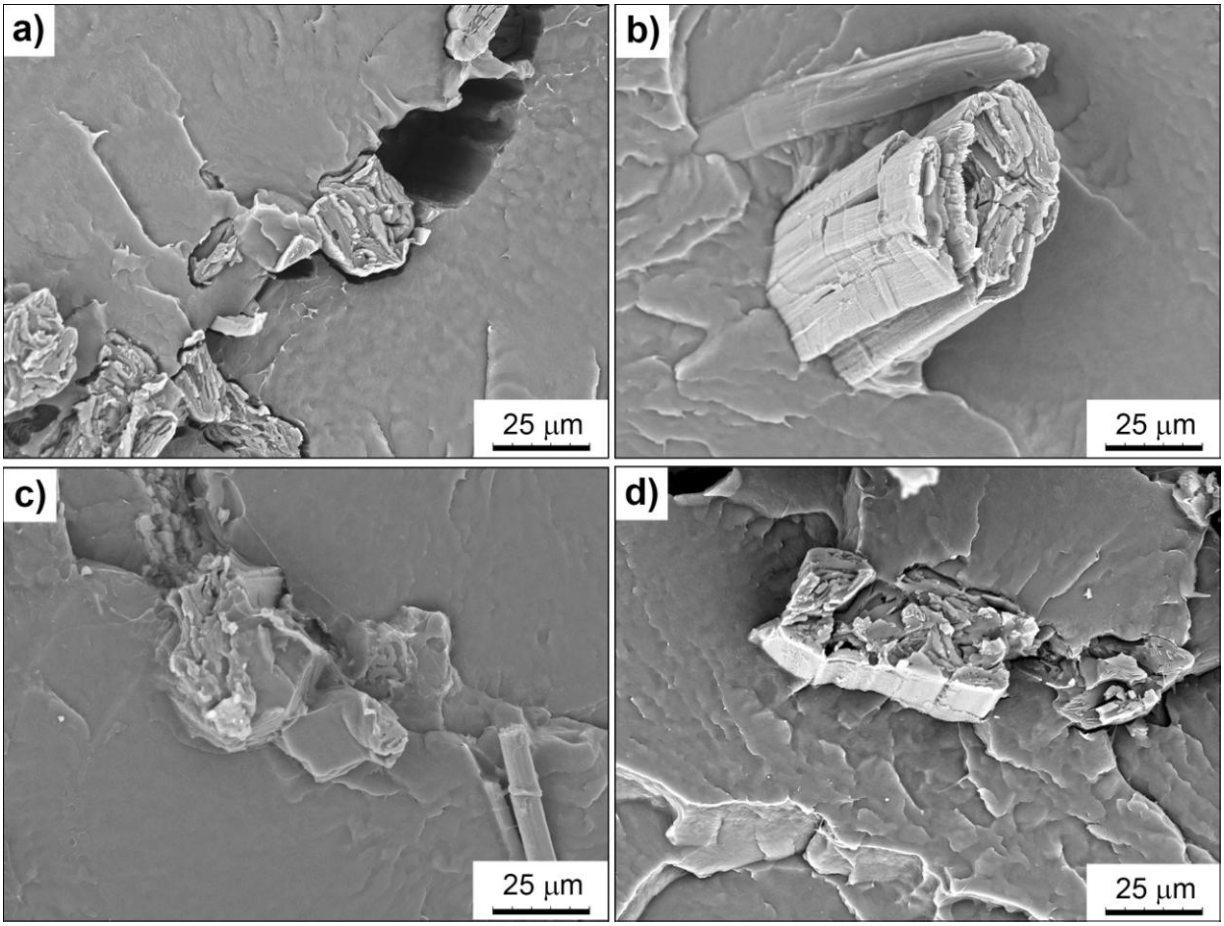


Fig. 10. SEM micrographs of preliminary PBAT-based composites containing < 5 wt.% of: (a) uncut HF, (b) HF_{Na}, (c) HF_{Na}-npMCO, and (d) HF_{Na}-C-pMCO fibres. (2-column fitting image)

Untreated HFs resulted very poorly adhered to the PBAT matrix (Fig. 10a). As shown in Fig. 10b, while the pre-treatment with NaOH improved fibre/matrix adhesion. The adhesion of the fibres to the PBAT matrix was noticeably further enhanced when HF_{Na}-npMCOs (Fig. 10c) or HF_{Na}-C-pMCOs (Fig. 10d) were used. No appreciable differences were evidenced between the two samples containing the fibres modified with the MCOs. This suggests that the macrocycles purification step and the subsequent addition of the catalyst prior to ED-ROP can be avoided, using directly the non-purified macrocycles as the compatibilizing agent.

On the basis of these preliminary results, PBAT-based composites containing higher amounts (about 40 wt.%) of uncut oriented HF, HF_{Na}, and HF_{Na}-npMCO fibres were prepared by

compression moulding through the two-steps method described in the Materials and methods section.

The ensuing eco-composites were then characterized by SEM microscopy to estimate fibre-matrix interaction and by performing uniaxial tensile tests to evaluate their mechanical properties.

SEM micrographs of Fig. 11 confirm the higher interaction of MCO-modified fibres (Fig. 11 b,d) with the PBAT matrix if compared to the poor one shown by untreated HF fibres (Fig. 11 a,c).

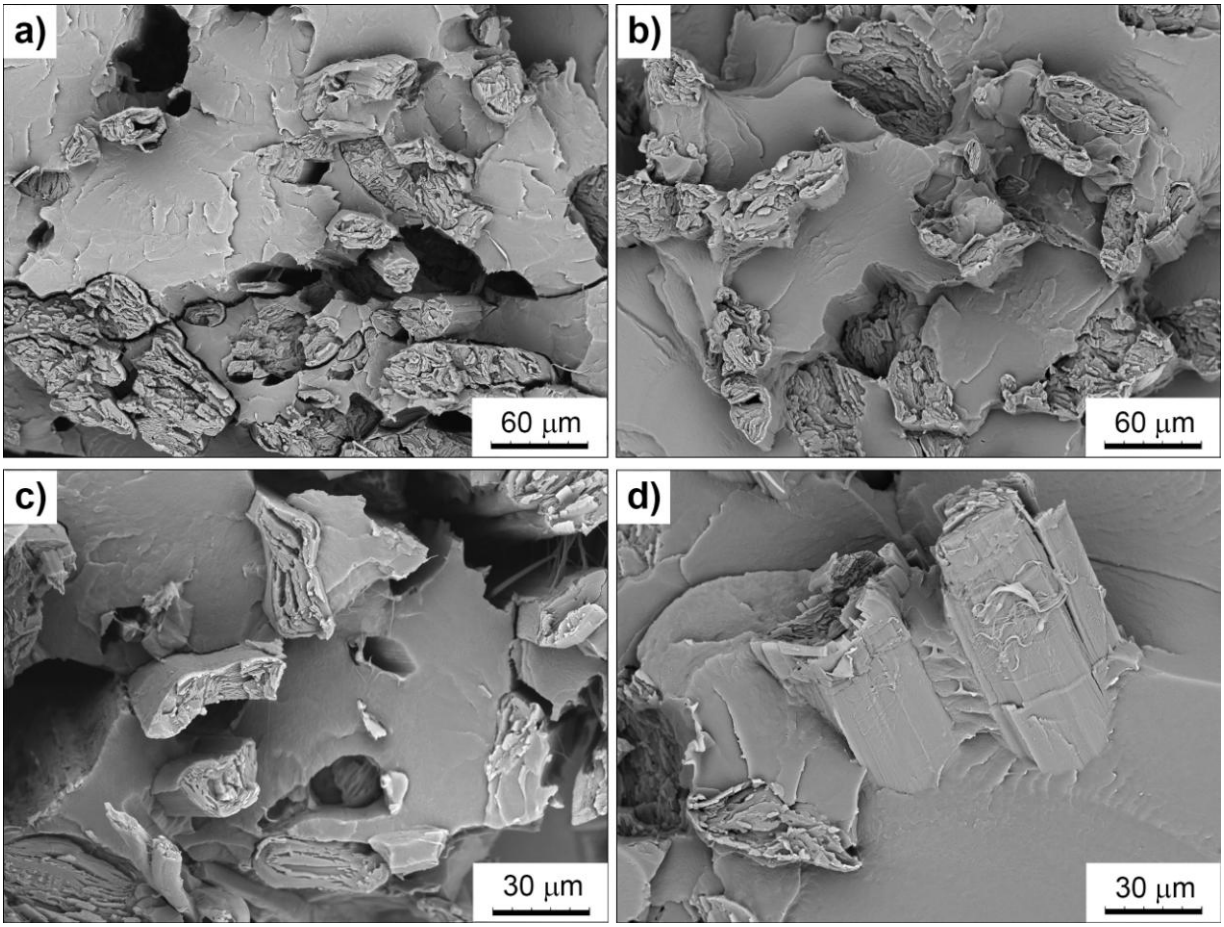


Fig. 11. SEM micrographs of PBAT-based composites containing: (a,c) uncut HF, and (b,d) HF_{Na}-npMCO fibres. (2-column fitting image)

Thermal stability of PBAT, HF fibres, and HF-PBAT composites was investigated by TGA analysis carried out in dynamic mode under nitrogen; the characteristic temperatures are reported in Table 4. A double step weight loss was observed in the TG curve of PBAT-based composites: the first step, between 300 and 400°C, corresponds to the thermal degradation of the hemp fibres (T_{onset1} and T_{Vmax1}), and the second one, in the range 400-500°C, is ascribable to the thermal degradation of the PBAT matrix (T_{onset2} and T_{Vmax2}). The degradation onset of the hemp fibres (about 340°C) was shifted toward higher temperatures (about 360°C) by their incorporation into the PBAT matrix.

On the other hand, the thermal degradation of the PBAT (T_{onset2}) in the composites is practically independent on the fibre added and slightly lower than that of neat PBAT.

Table 4. T_{onset} and T_{Vmax} decomposition temperatures of hemp fibres, neat PBAT, and PBAT/hemp fibres eco-composites determined by TGA at 10°C/min under N_2.

Sample	T_{onset1} (°C)	T_{Vmax1} (°C)	T_{onset2} (°C)	T_{Vmax2} (°C)
PBAT	-	-	385	418
PBAT + HF	361	384	372	422
PBAT + HF_{Na}	353	378	375	425
PBAT + HF_{Na}-npMCO	357	384	362	419

The mechanical properties of these PBAT-based composites were evaluated by uniaxial tensile tests; the results (Table 5) were normalized with respect to the effective amount of fibres in the composite sample, as determined by TGA. The presence of the fibres resulted in a great increase in storage modulus (E) and stress at break (σ_b) values when compared to those of the neat PBAT. Correspondingly, the composite samples are more brittle, as evidenced by the remarkable reduction of the elongation at break (ε_b).

Table 5. Tensile modulus (E), stress (σ_b) and strain (ε_b) at break obtained for neat PBAT and PBAT-based composites containing about 40 wt.% hemp fibres.

Sample	E (MPa)	σ_b (MPa)	ε_b (%)
PBAT	75 ± 8	24 ± 2	1527 ± 86
PBAT + HF	2435 ± 249	111 ± 14	12 ± 1
PBAT + HF_{Na}	4805 ± 550	97 ± 12	4 ± 1
PBAT + HF_{Na}-npMCO	5480 ± 280	76 ± 14	2 ± 0.3

Among the composites, the sample containing the MCO-modified fibres (PBAT + HF_{Na}-npMCO) revealed the highest E value, indicative of the beneficial effect of such modification on the fibre-matrix adhesion, which in turn promotes under loading an efficient stress transfer from matrix to the fibrous reinforcement. The slight decrease of the stress at break could be ascribed to a mechanical weakening of the hemp fibres due to the thermal treatment carried out during the ED-ROP reaction (190°C, 30 min). Even though a TGA isothermal analysis carried out at 200°C in O_2 atmosphere for

30 min revealed a good thermo-oxidative resistance of HF_{Na}s fibres (the weight loss is about 0.5%), the maintenance at high temperature in oxidative atmosphere could be slightly detrimental to the mechanical properties of the fibres, as reported by Prasad *et al.* [34].

Dynamic-mechanical analysis (DMA) of PBAT and PBAT-based composites containing HF_{Na} and HF_{Na}-npMCO fibres was carried out to evaluate the effective reinforcement exerted by the fibres in terms of elastic or storage modulus (G'). The resulting curves are shown in Fig. 12a. The presence of the long fibres in the composites resulted in a strong increase of the mechanical properties with respect to those of the neat PBAT (G' at 1Hz = 47 MPa). As expected, this effect is more pronounced along the fibre axis than in the orthogonal direction: in fact, the values of G' measured at 1Hz are respectively 510 and 260 MPa for the PBAT + HF_{Na} composite, and the corresponding values for PBAT + HF_{Na}-npMCO are 770 and 320 MPa. The beneficial effect of the MCO-functionalization of HFs with respect to the simple alkali treatment is evidenced by an increase in G' of the 51% in the longitudinal direction and 23% in the transversal one.

The effectiveness of the compatibilization through MCOs is also visible in the FE-SEM micrograph of the PBAT + HF_{Na}-npMCO sample taken after DMA analysis and reported in Fig. 12b. Besides fibres detached from the matrix, as a consequence of the torsional strain, the fibre external layer remain adhered to the polymer, indicating the good adhesion between the HF-modified surface and the PBAT matrix.

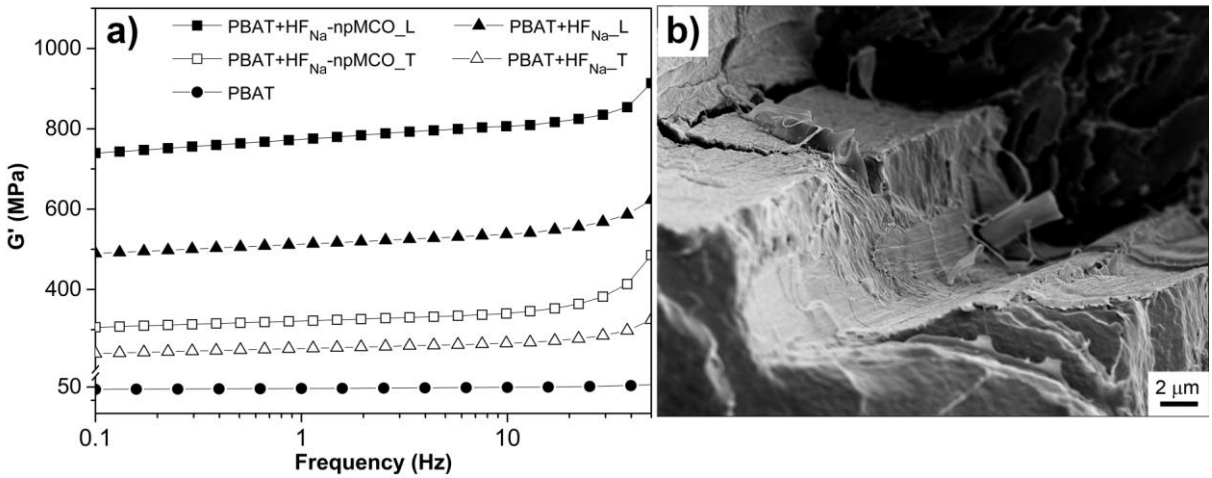


Fig. 12. (a) DMA curves of PBAT, PBAT + HF_{Na} and PBAT + HF_{Na}-npMCO samples obtained in longitudinal (L) and transversal (T) directions; (b) FE-SEM micrograph of PBAT + HF_{Na}-npMCO sample after DMA analysis. (2-column fitting image)

4. Conclusions

CDP of poly(1,4-butylene adipate-*co*-terephthalate) (PBAT) was, for the first time, successfully performed at high dilution, in mild conditions and in the presence of a suitable transesterification catalyst, achieving quantitative yields of the corresponding macrocyclic oligomers (MCOs).

The reconversion of the MCOs into linear polymeric chains was successfully accomplished by ED-ROP, carried out by simply heating the neat macrocycles as obtained from CDP, without any further addition of catalyst.

ED-ROP of the MCOs adsorbed onto hemp fibres previously mildly treated with acqueous NaOH to remove non-cellulosic and amorphous components and favour accessibility to the functional groups, led to modified fibres with anchored PBAT oligomers, that is to a perfectly suited compatibilizing agent for PBAT composites reinforced with hemp fibres.

PBAT-based composites containing about 40 wt.% of pristine, NaOH-treated, and MCO-modified hemp fibres were prepared by compression moulding. The sample compatibilized with the MCO-modified fibres showed the best fibre/matrix adhesion, which resulted in enhanced mechanical properties in terms of elastic modulus with respect to not only the neat PBAT but also to the other composites.

The overall results gathered so far validate the compatibilization strategy adopted for preparing eco-friendly composite materials based on a biodegradable polyester matrix reinforced with high amounts of low cost fibres arising from hemp manufacturing by-products.

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References

[1] P. Hodge, Entropically driven ring-opening polymerization of strainless organic macrocycles, Chem. Rev. 114 (2014) 2278-2312.

[2] P. Hodge, Recycling of condensation polymers via ring-chain equilibria, Polym. Adv. Technol. 26 (2015) 797-803.

[3] L. Conzatti, R. Utzeri, P. Hodge, P. Stagnaro, A novel tin-based imidazolium-modified montmorillonite catalyst for the preparation of poly(butylene terephthalate)-based nanocomposites using in situ entropically-driven ring-opening polymerization, RSC Adv. 5 (2015) 6222-6231.
[4] P. Hodge, Cyclodepolymerization as a method for the synthesis of macrocyclic oligomers, React. Funct. Polym. 80 (2014) 21-32.
[5] D.J. Brunelle, Macrocycles for the synthesis of high molecular weight polymers, in: J.R. Ebdon, G.C. Eastmond (Eds.), New methods of polymer synthesis - vol. 2, Blackie, London, 1995, pp. 197-235.
[6] A. Ben-Haida, H.M. Colquhoun, P. Hodge, J.L. Stanford, A novel approach to processing high-performance polymers that exploits entropically-driven ring-opening polymerization, Macromol. Rapid Comm. 26 (2005) 1377-1382.
[7] M. Alessi, L. Conzatti, P. Hodge, S. Taglialatela Scafati, P. Stagnaro, A possible means to assist the processing of PET, PTT and PBT, Macromol. Mater. Eng. 295 (2010) 374-380.
[8] M.N. Belgacem, A. Gandini, Monomers, polymers and composites from renewable resources, Elsevier, Oxford UK, 2008.
[9] O. Faruk, A.K. Bledzki, H.P. Fink, M. Sain, Biocomposites reinforced with natural fibers: 2000-2010, Prog. Polym. Sci. 37 (2012) 1552-1596.
[10] M.P.M. Dicker, A.B. Baker, P.F. Duckworth, A.B. Baker, G. Francois, M.K. Hazzard, P.M. Weaver, Green composites: A review of material attributes and complementary applications, Compos. Part A-Appl. S. 56 (2014) 280-289.
[11] T. Gurunathan, S. Mohanty, S. K. Nayak, A review of the recent developments in biocomposites based on natural fibres and their application perspectives, Compos. Part A-Appl. S., 77 (2015) 1-25.
[12] K. L. Pickering, M. G. Aruan Efendy, T. M. Le, A review of recent developments in natural fibre composites and their mechanical performance, Compos. Part A-Appl. S. 83 (2016) 98-112.
[13] S. Kalia, B.S. Kaith, I. Kaur, Pretreatments of natural fibers and their application as reinforcing material in polymer composites - A review, Polym. Eng. Sci., 49 (2009) 1253-1272.
[14] L. Conzatti, F. Giunco, P. Stagnaro, M. Capobianco, M. Castellano, E. Marsano, Polyester-based biocomposites containing wool fibres, Compos. Part A-Appl. S. 43 (2012) 1113-1119.
[15] L. Conzatti, F. Giunco, P. Stagnaro, A. Patrucco, C. Marano, M. Rink, E. Marsano, Composites based on polypropylene and short wool fibres, Compos. Part A-Appl. S. 47 (2013) 165-171.

585 [16] L. Conzatti, F. Giunco, P. Stagnaro, A. Patrucco, C. Tonin, C. Marano, M. Rink, E. Marsano,
586 Wool fibres functionalised with a silane-based coupling agent for reinforced polypropylene
587 composites, Compos. Part A-Appl. S. 61 (2014) 51-59.
588 [17] L. Conzatti, R. Utzeri, P. Hodge, P. Stagnaro, Biodegradable polyester-based eco-composites
589 containing hemp fibers modified with macrocyclic oligomers, AIP Conference Proceedings 1736,
590 (2016) 020126.
591 [18] L.Y. Mwaikambo, M.P. Ansell, Mechanical properties of alkali treated plant fibres and their
592 potential as reinforcement materials. I. hemp fibres, J Mater. Sci. 41 (2006) 2483-2496.
593 [19] L.E. Hult, T. Iversen, J. Sugiyama, Characterization of the supramolecular structure of
594 cellulose in wood pulp fibres, Cellulose 10 (2003) 103-110.
595 [20] C.J. Garvey, I.H. Parker, G.P. Simon,On the interpretation of X-ray diffraction powder patterns
596 in terms of the nanostructure of cellulose I fibres. Macromol. Chem. Phys. 206 (2005) 1568-1575.
597 [21] S.D. Kamau, P. Hodge, M. Helliwell, Cyclo-depolymerization of poly(propylene
598 terephthalate): Some ring-opening polymerizations of the cyclic oligomers produced, Polym. Adv.
599 Technol. 14 (2003) 492-501.
600 [22] X. Li, L.G. Tabil, S. Panigrahi, Chemical treatments of natural fiber for use in natural fiber-
601 reinforced composites: A review, J. Polym. Environ. 15 (2007) 25-33.
602 [23] R. Agrawal, N.S. Saxena, K.B. Sharma, S. Thomas, M.S. Sreekala, Activation energy and
603 crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde
604 composites, Mat. Sci. Eng. A 277 (2000) 77-82.
605 [24] T. Fisher, M. Hajaligol, B. Waymack, D. Kellogg, Pyrolysis behavior and kinetics of biomass
606 derived materials, J. Anal. Appl. Pyrol. 62 (2002) 331-349.
607 [25] C.M. Popescu, M.C. Popescu, C. Vasile, Structural analysis of photodegraded lime wood by
608 means of FT-IR and 2D IR correlation spectroscopy, Int. J. Biolog. Macromol., 48 (2011) 667-675.
609 [26] K.K. Pandey, A study of chemical structure of soft and hardwood and wood polymers by FTIR
610 spectroscopy, J. Appl. Polym. Sci. 71 (1999) 1969-1975.
611 [27] K. Bilba, M.A. Arsene, A. Ouensanga, Study of banana and coconut fibers - Botanical
612 composition, thermal degradation and textural observations, Biores. Technol. 98 (2007) 58-68.
613 [28] C.J. Garvey, I.H. Parker, G.P. Simon, On the interpretation of X-ray diffraction powder
614 patterns in terms of the nanostructure of cellulose I fibres, Macromol. Chem. Phys. 206 (2005)
615 1568-1575.
616 [29] S. Park, J.O. Baker, M.E. Himmel, P.A. Parilla, D.K. Johnson, Cellulose crystallinity index:
617 measurement techniques and their impact on interpreting cellulase performance, Biotechnol.
618 Biofuels, 3 (2010).

[30] S. Ouajai, R.A., Shanks, Composition, structure and thermal degradation of hemp cellulose after chemical treatments, Polym. Degrad. Stab. 89 (2005) 327-335.

[31] G.W. Beckermann, K.L. Pickering, Engineering and evaluation of hemp fibre reinforced polypropylene composites: Fibre treatment and matrix modification, Composites: Part A 39 (2008) 979-988.

[32] M.A. Sawpan, K.L. Pickering, A. Fernyhough, Effect of various chemical treatments on the fibre structure and tensile properties of industrial hemp fibres, Composites: Part A 42 (2011) 888-895.

[33] V. Tserki, N.E. Zafeiropoulos, F. Simon, C. Panayiotou, A study of the effect of acetylation and propionylation surface treatments on natural fibres, Compos. Part A-Appl. S. 36 (2005) 1110-1118.

[34] B. M. Prasad, M. M. Sain, Mechanical properties of thermally treated hemp fibers in inert atmosphere for potential composite reinforcement, Mat. Res. Innovat. 7 (2003) 231-238.

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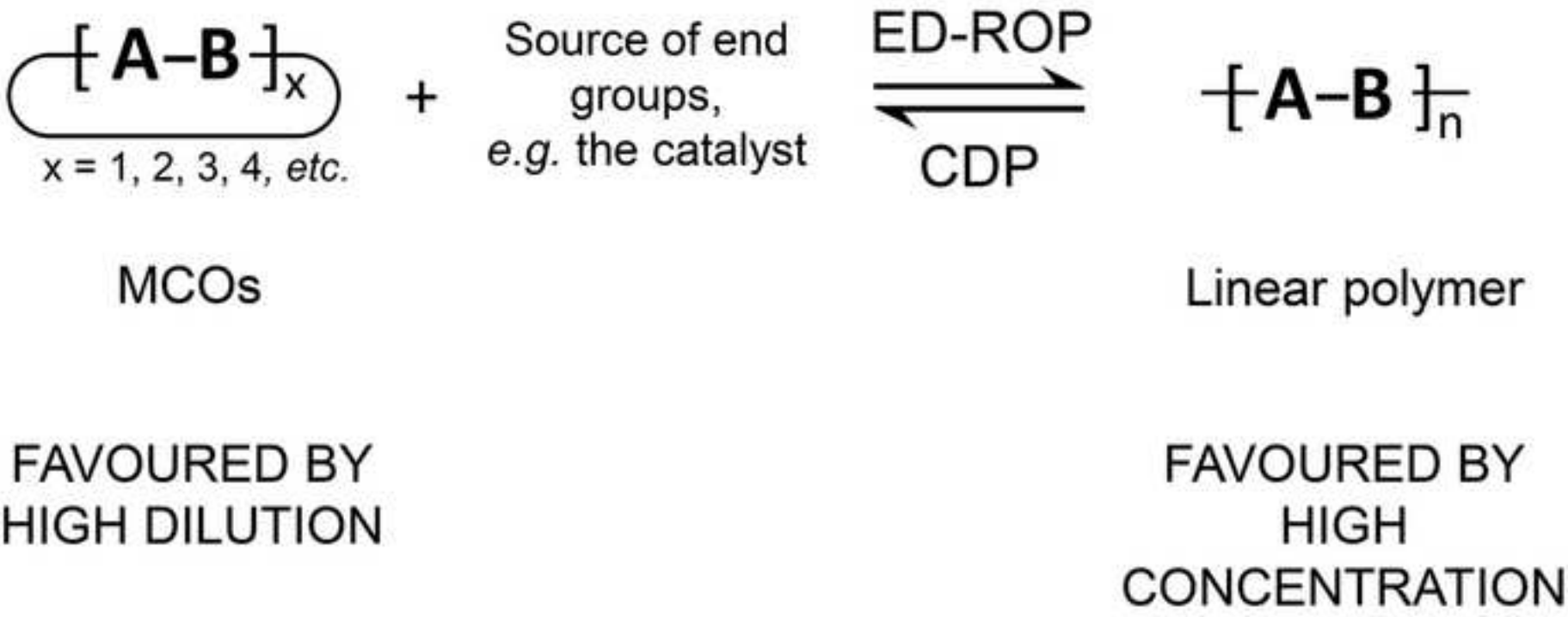

Scheme 2

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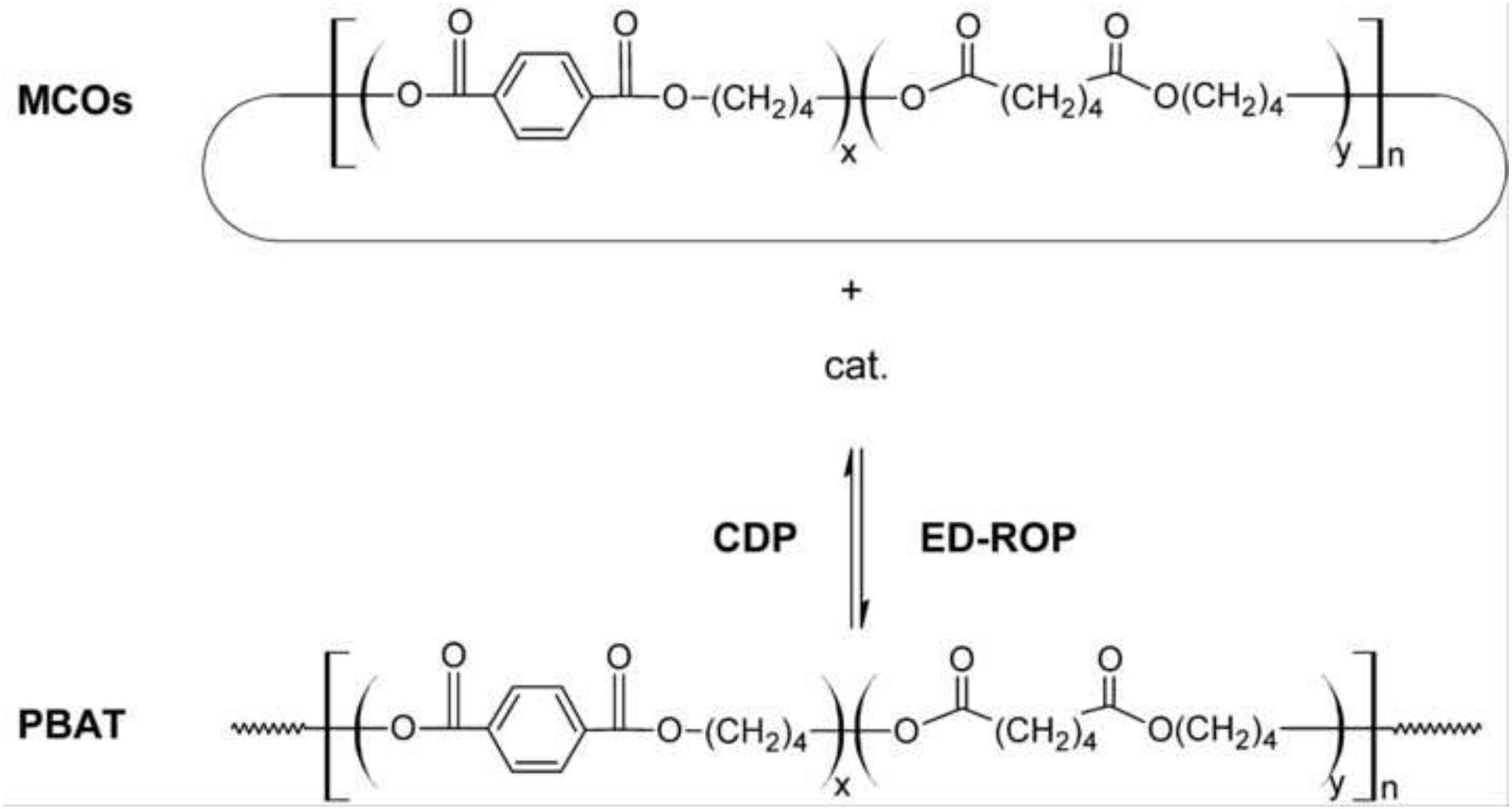

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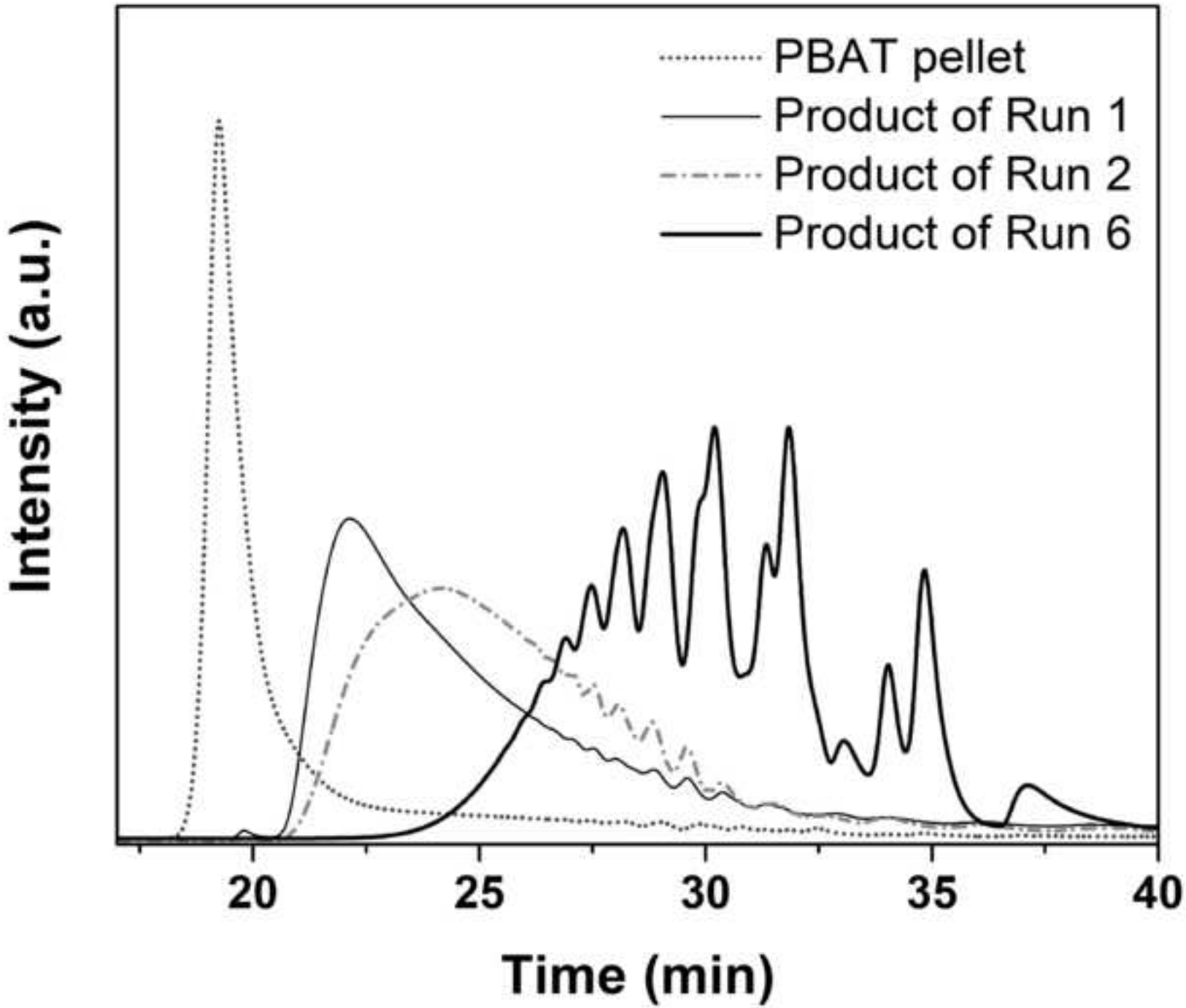

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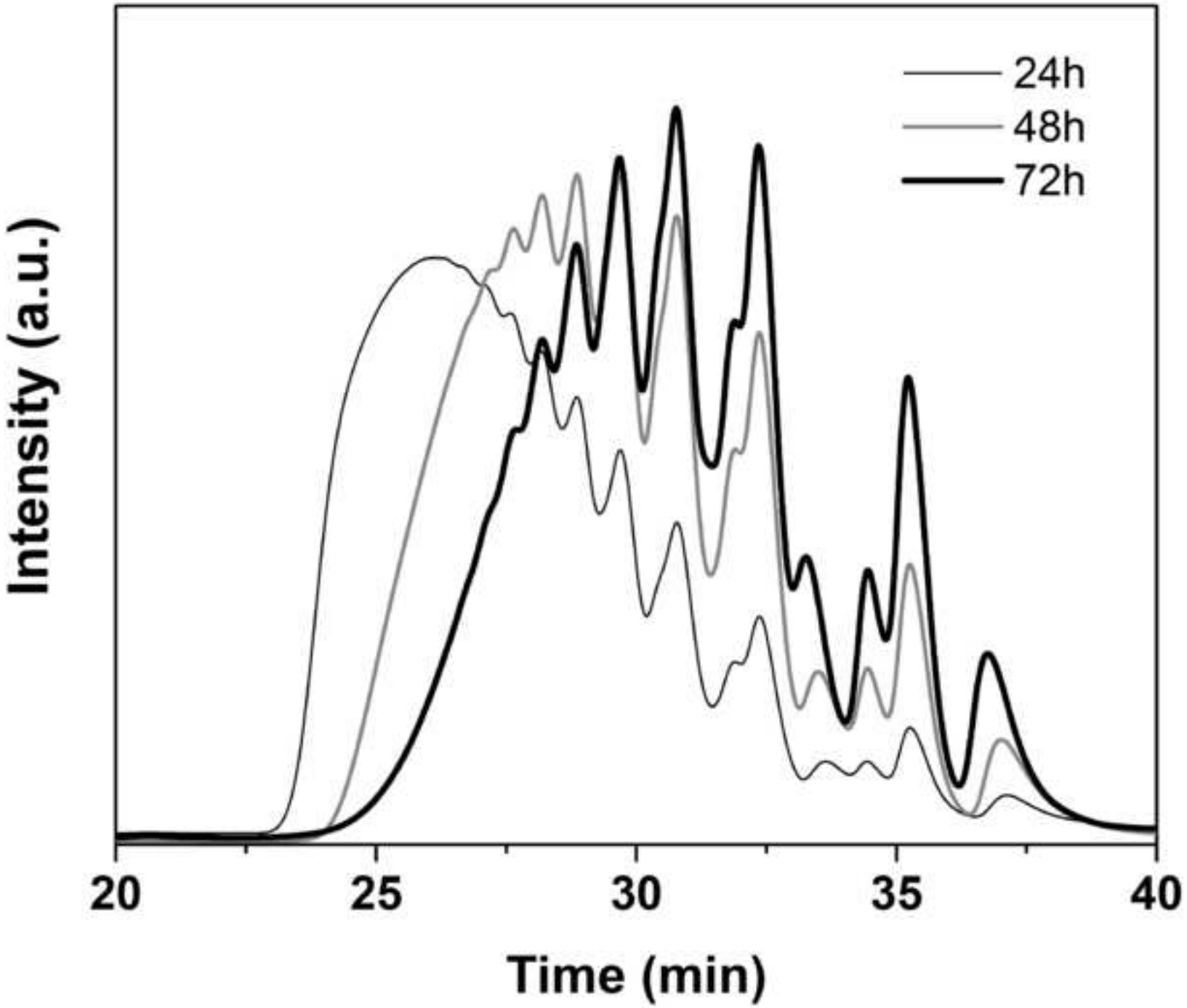

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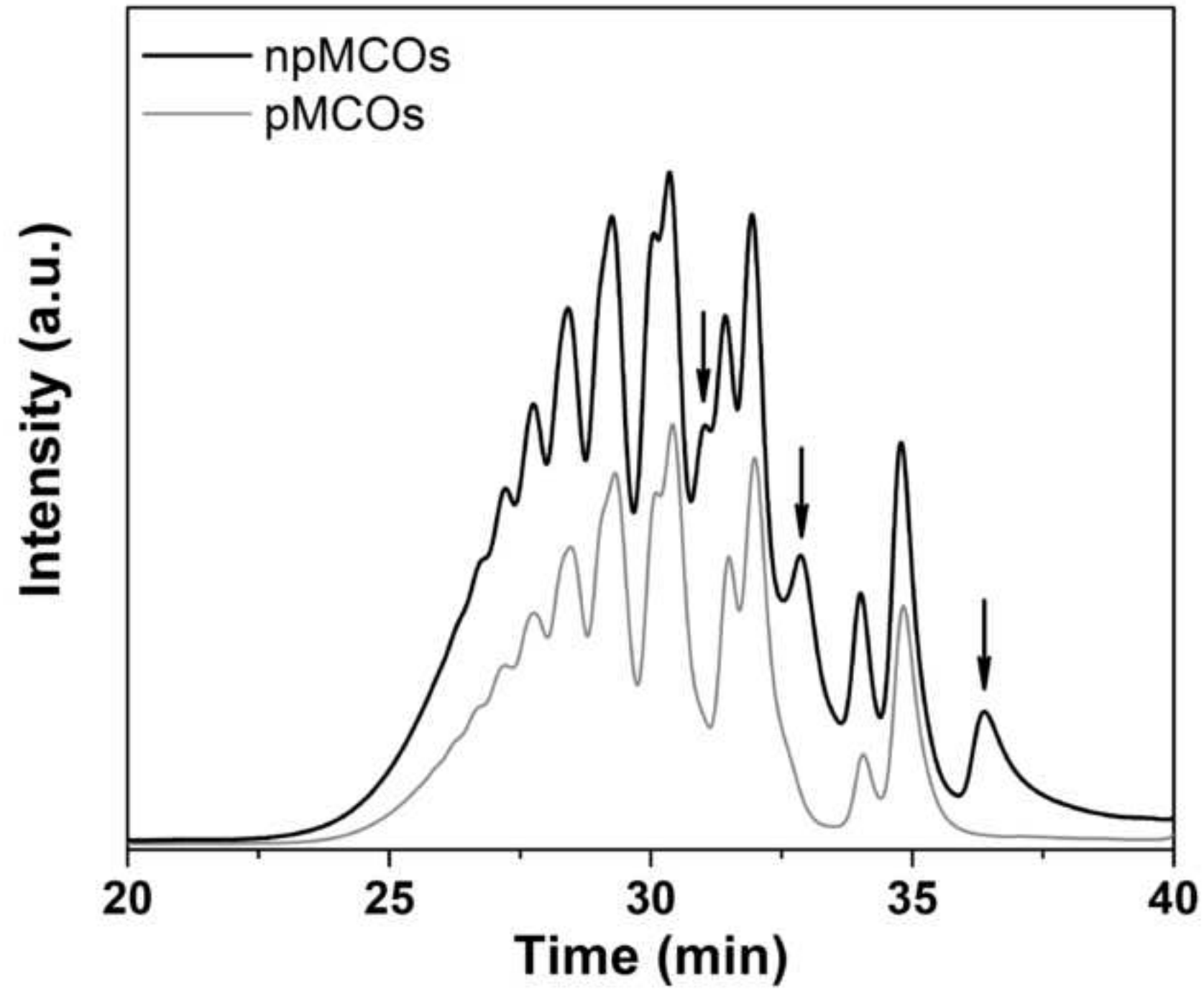

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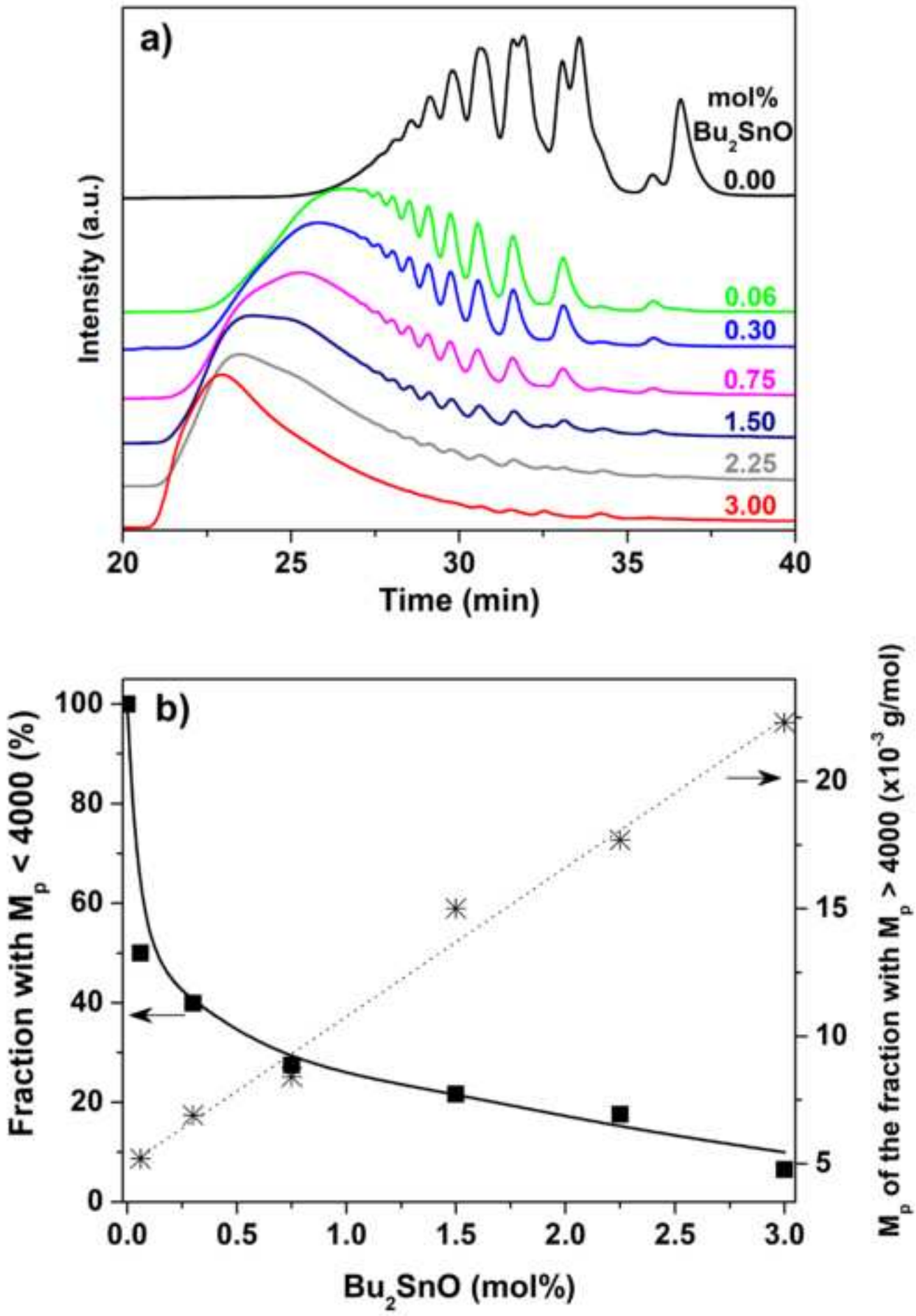

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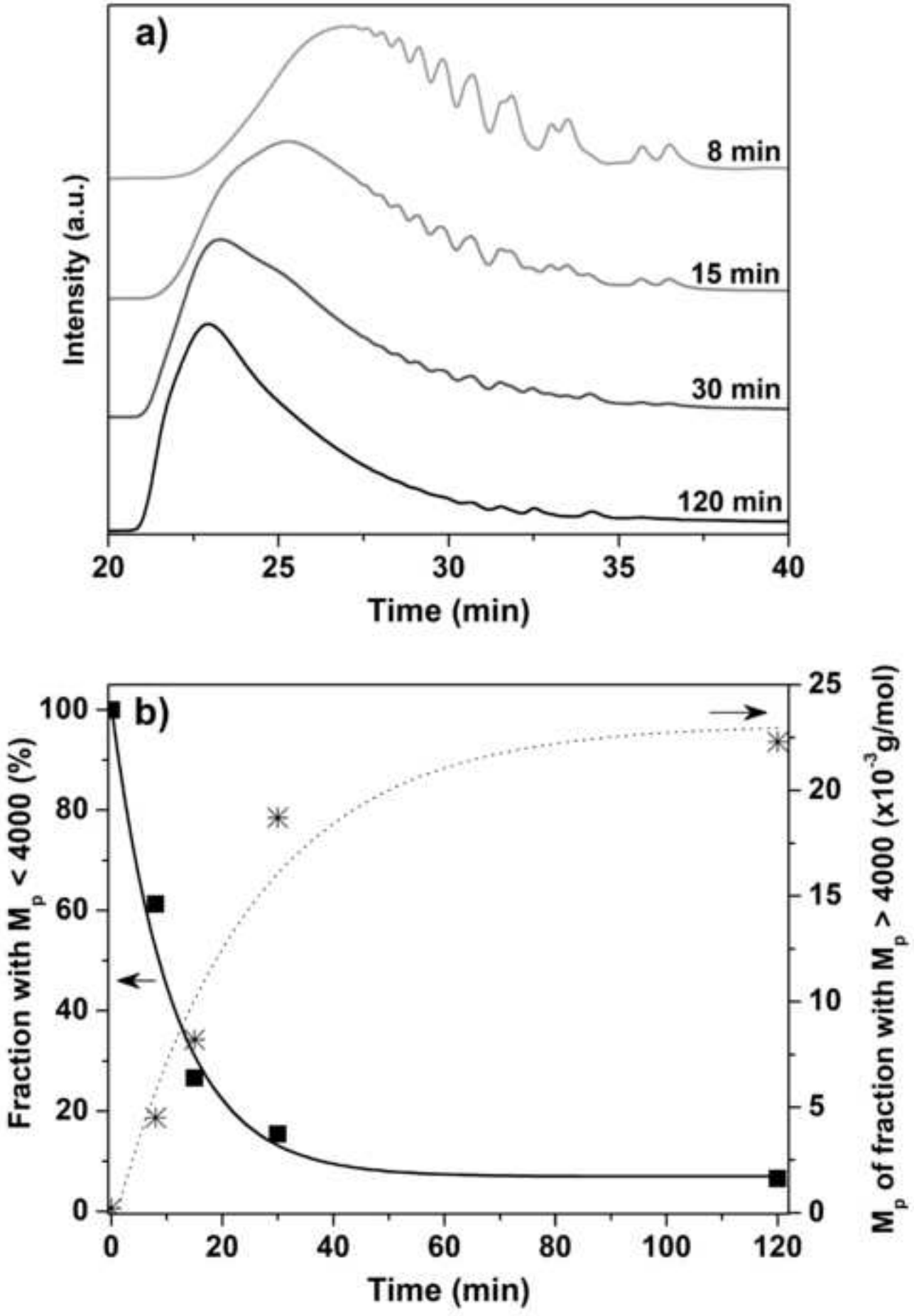

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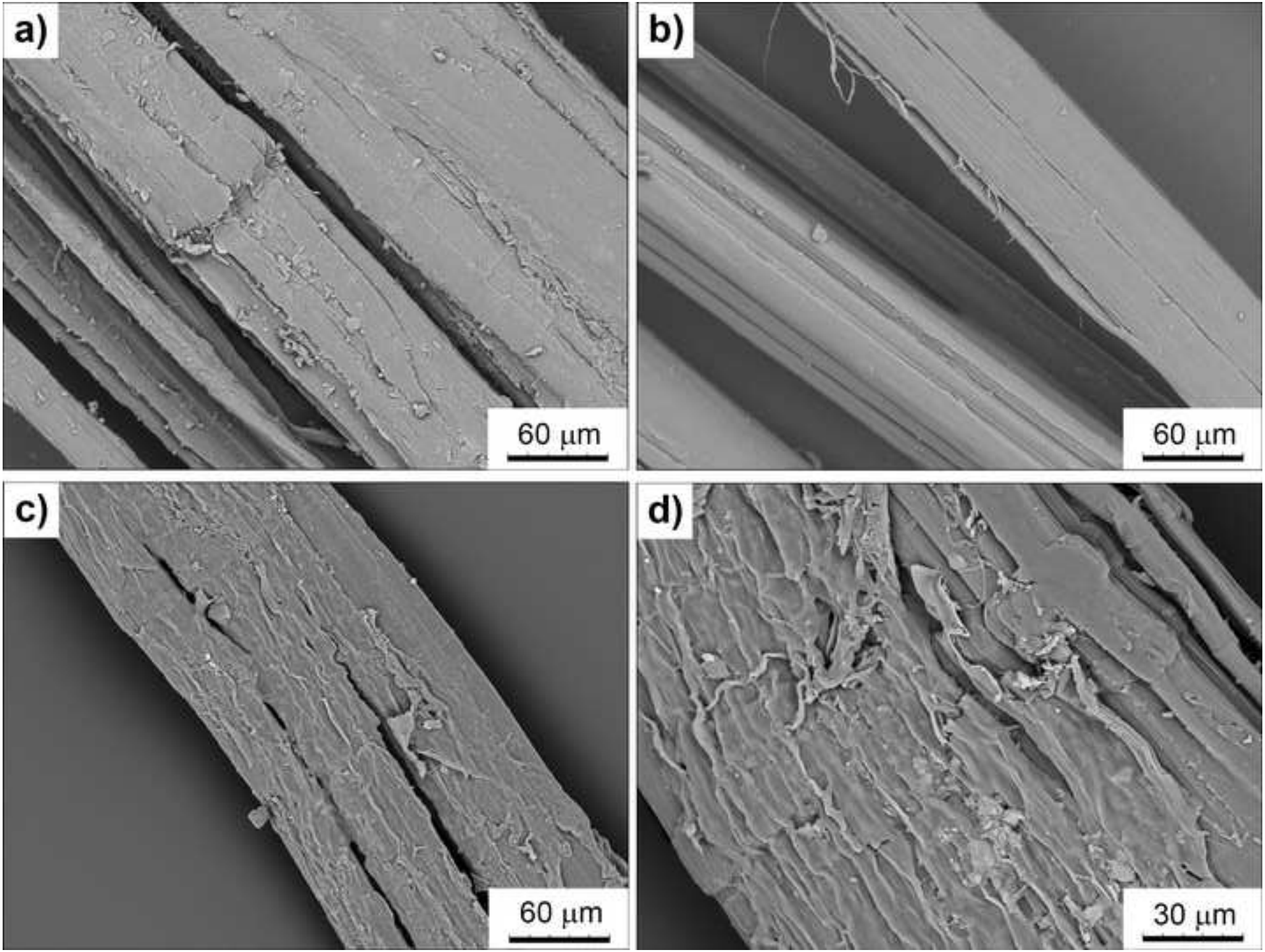

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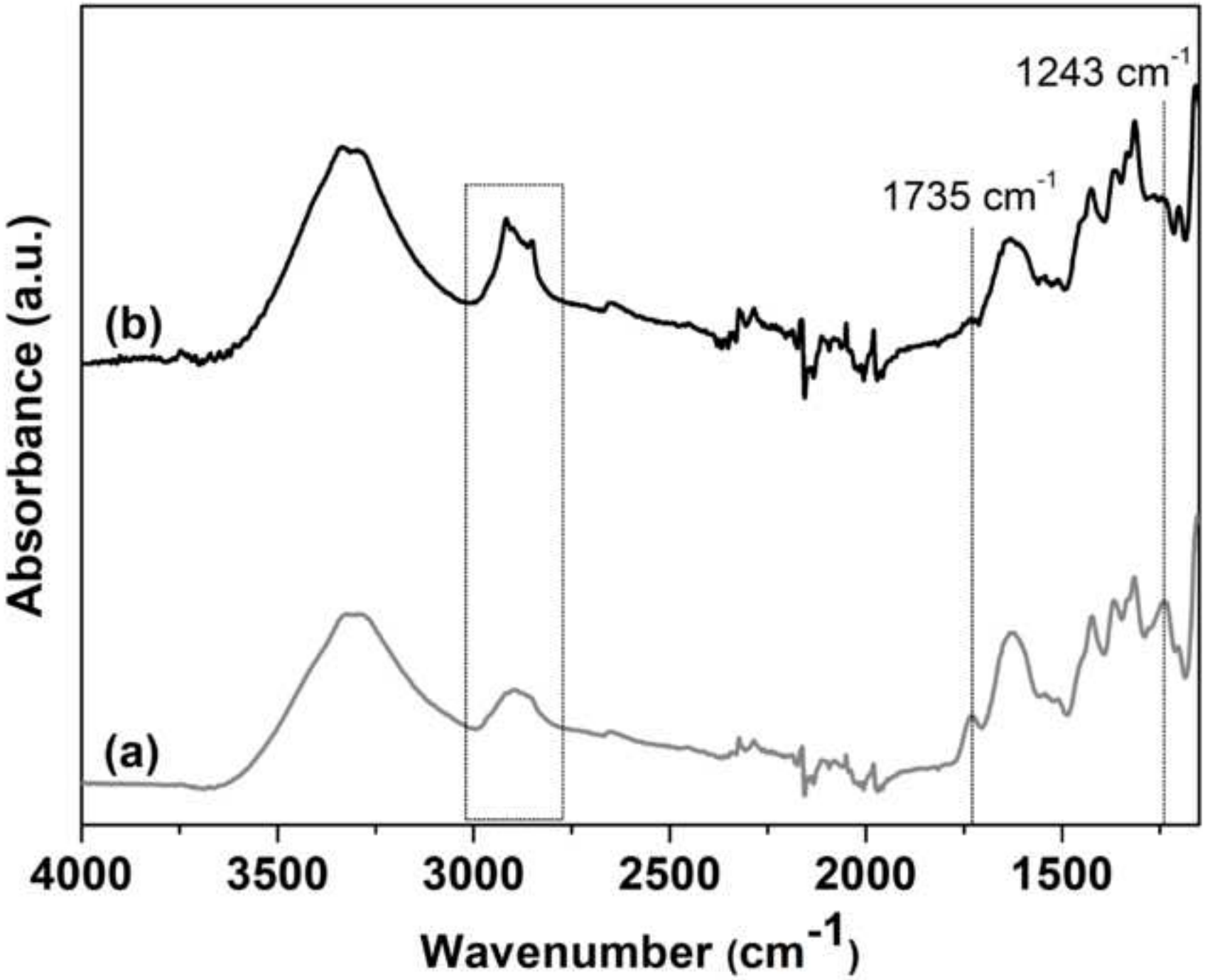

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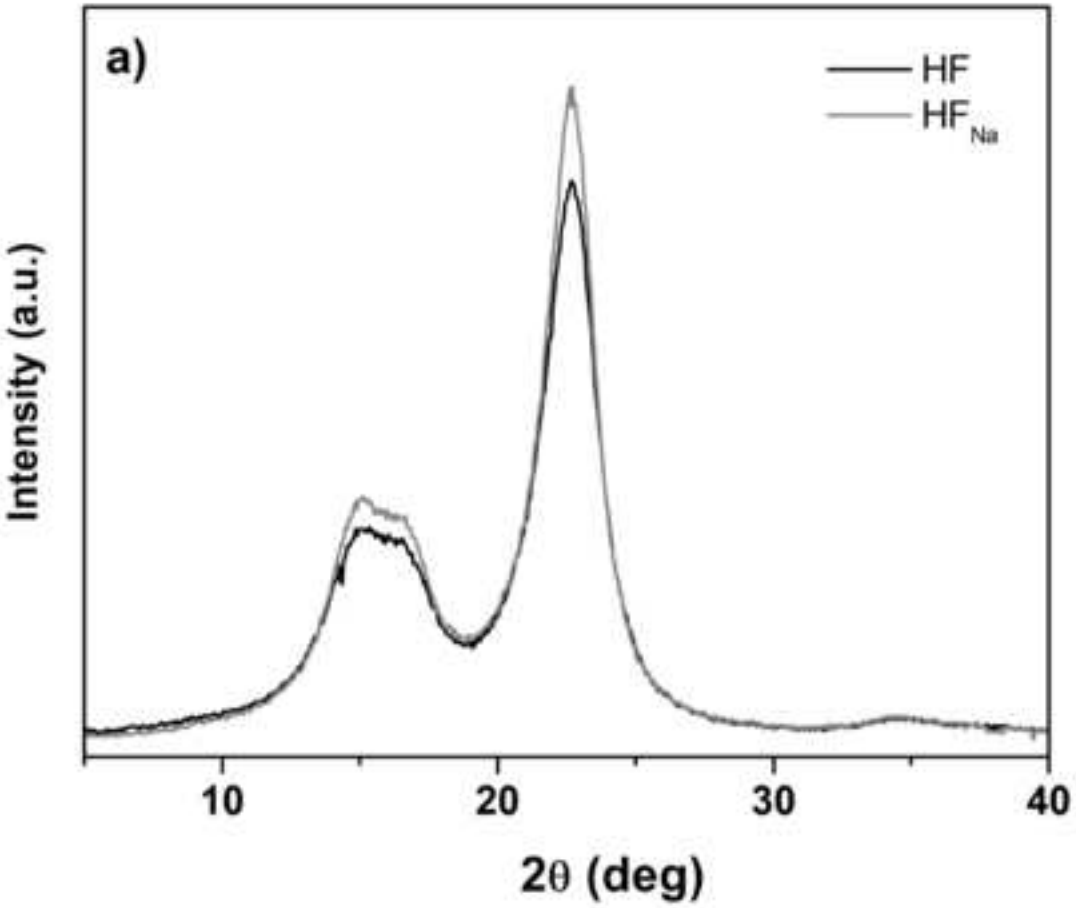

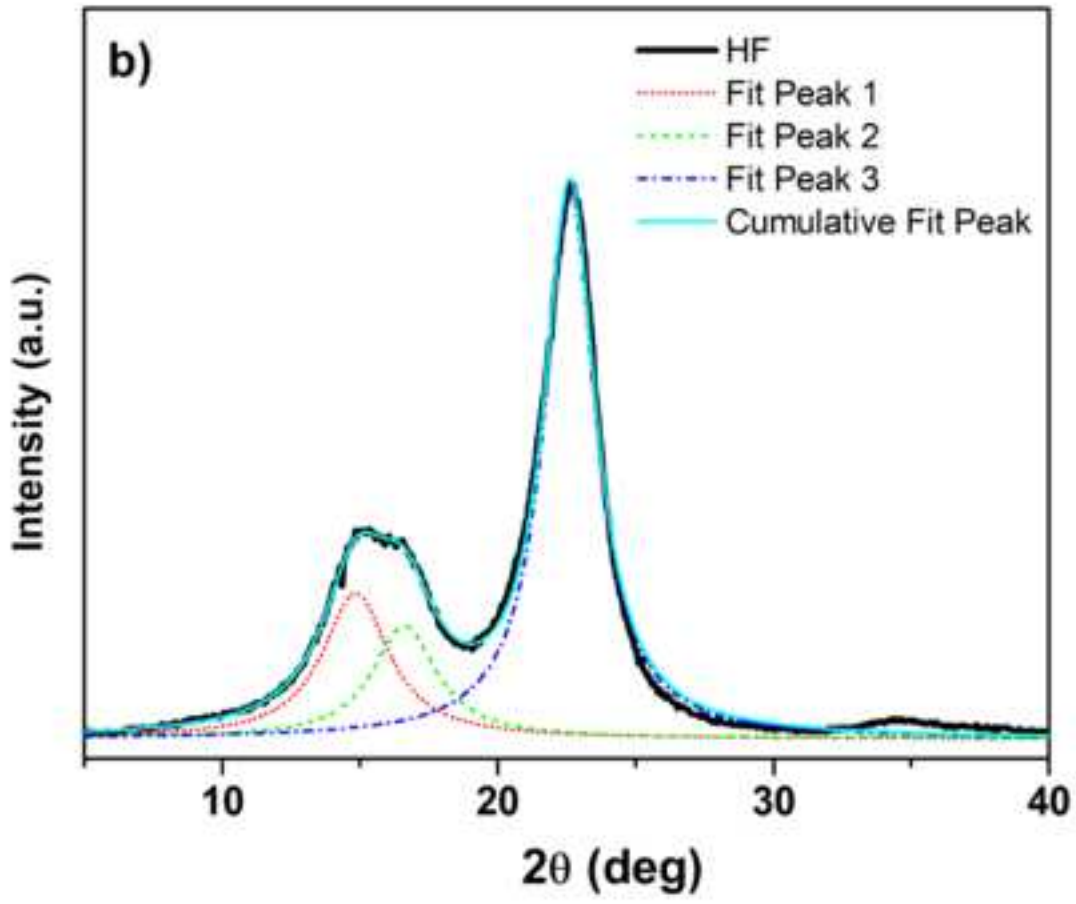

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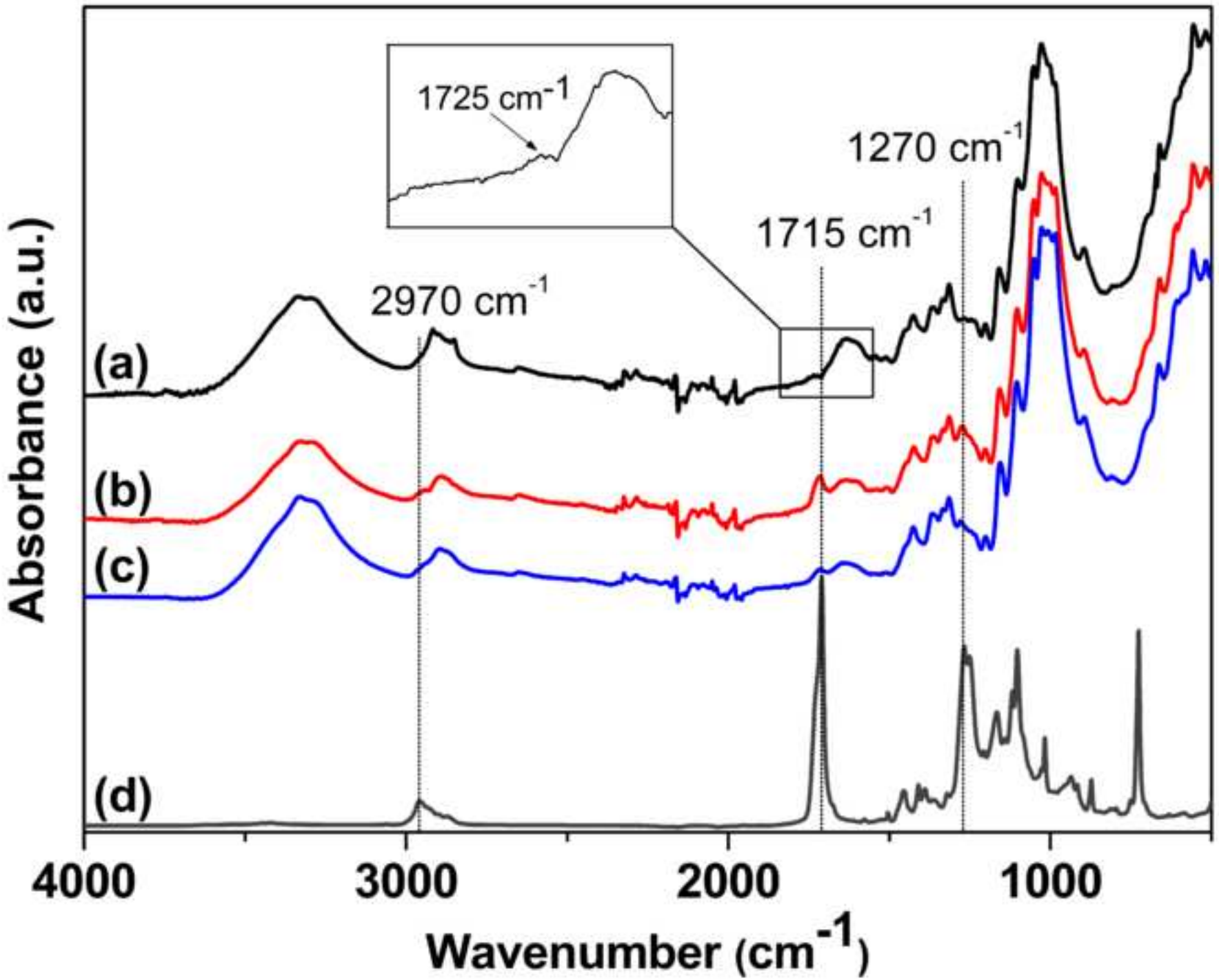

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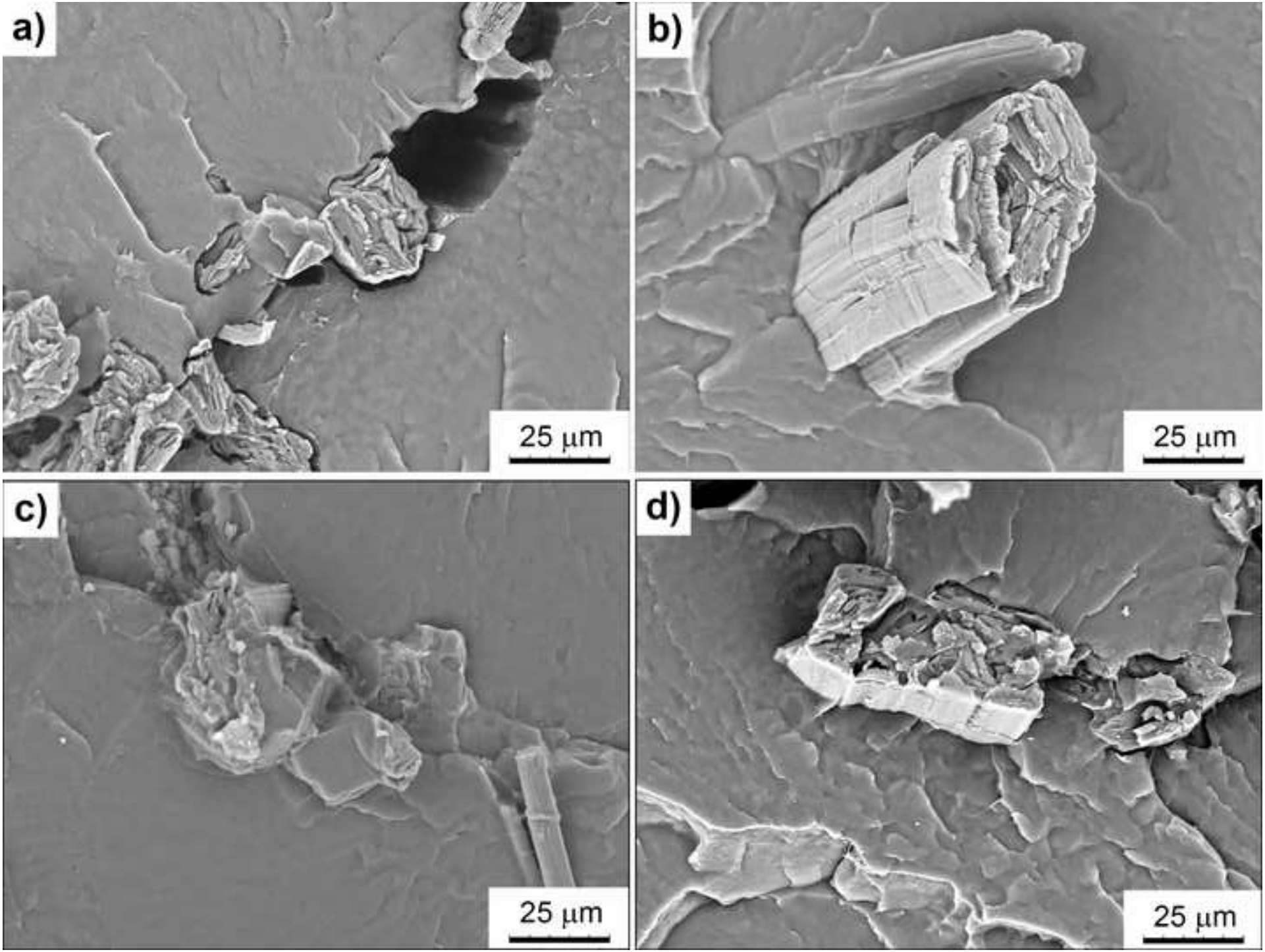

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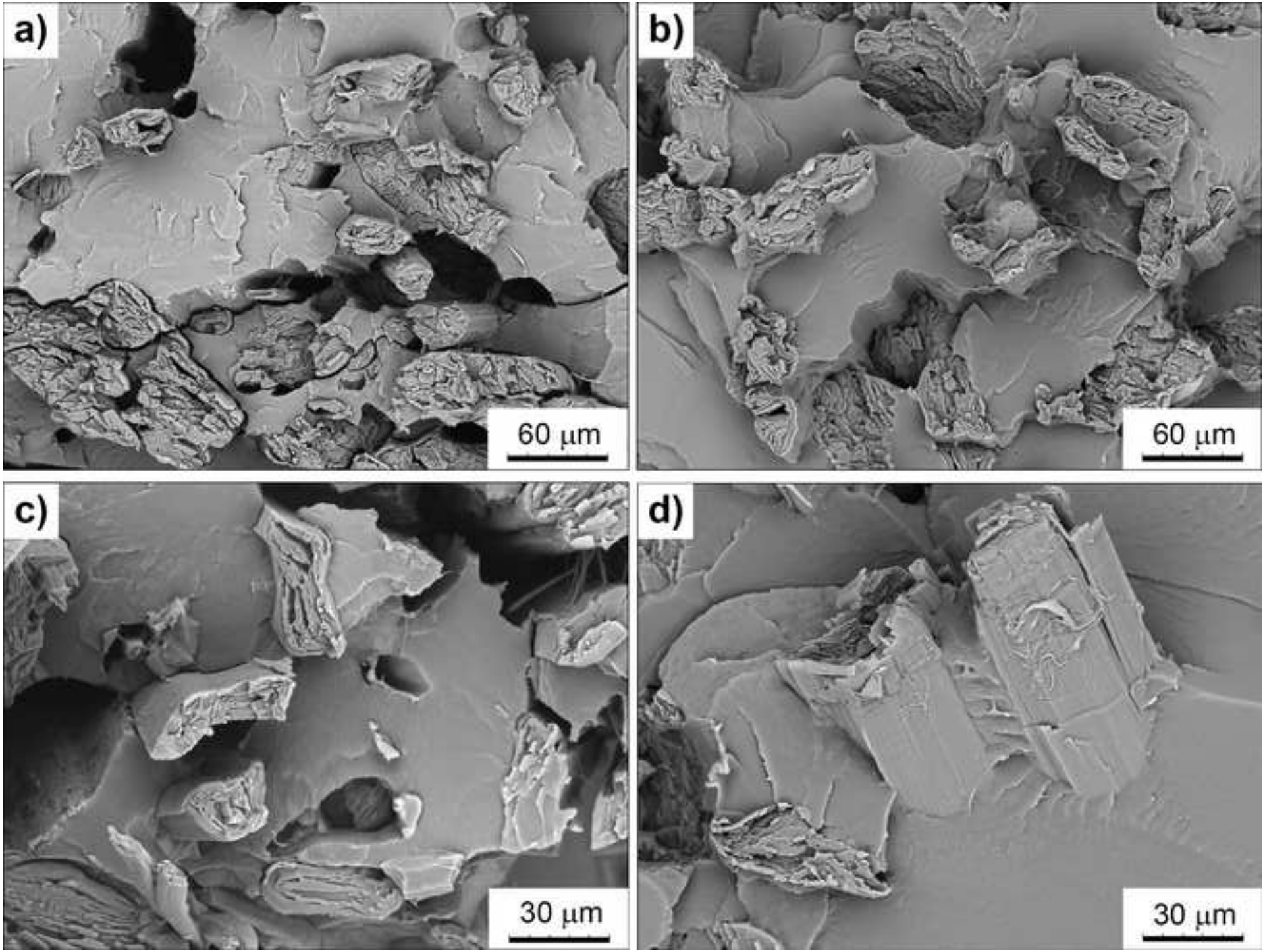

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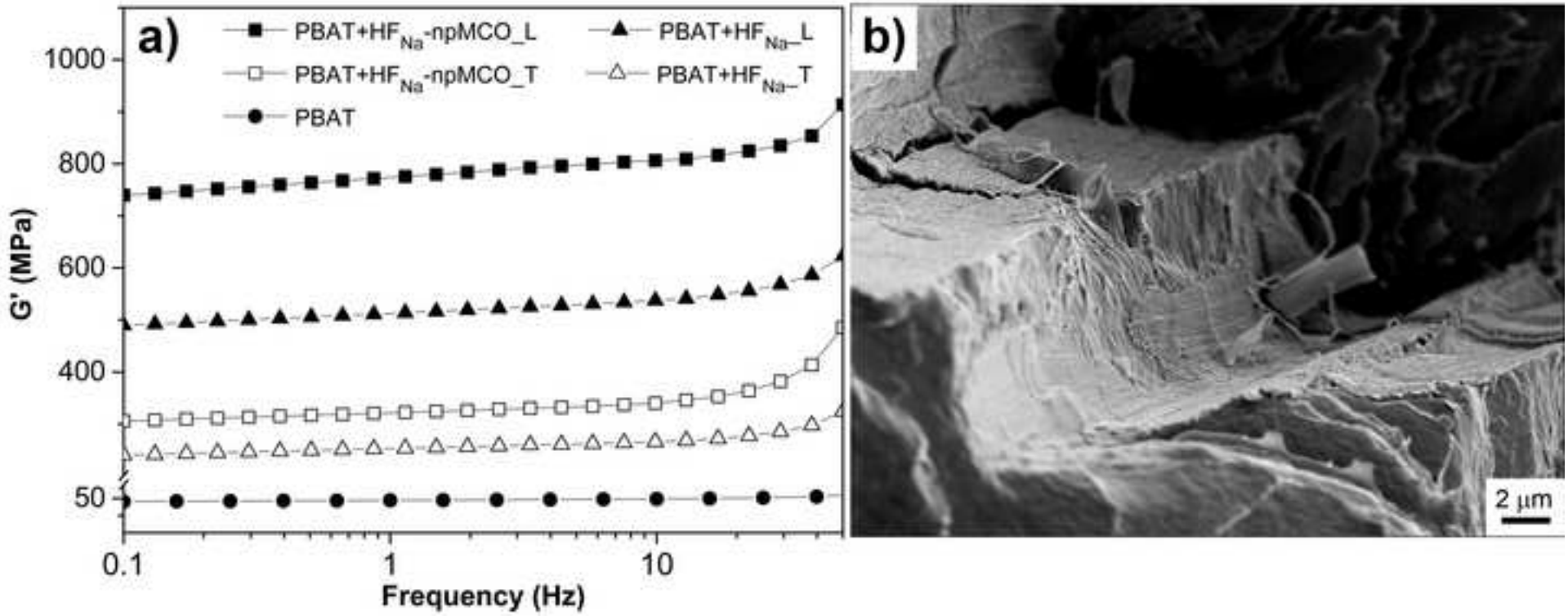

Highlights

- Macrocyclic oligomers (MCOs) easily obtained by cyclo-depolymerization of PBAT polyester
- The MCOs easily underwent entropically driven ring opening polymerization (ED-ROP)
- Low cost hemp fibres efficiently modified with the MCOs via ED-ROP
- Good fibre/matrix adhesion in PBAT composites containing MCO-modified hemp fibres
- Good mechanical performance of the PBAT/modified hemp fibres biodegradable eco-composites