Keratin based thermoplastic biocomposites: a review

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REVIEW PAPER

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Abstract Fibre reinforced composites have become important materials for manufacturing a diverse range of industrial products. Keratin-rich materials including sheep wool and poultry feathers can have added value by partially substituting synthetic polymers in the production of biocomposites with improved mechanical properties. The strong intermolecular disulfides, hydrogen, ionic and hydrophobic interactions of keratin make it behave as a thermoset material which is not easy to process and thermally blend with other polymers. Therefore, different plasticizers, compatibilizers and coupling agents were investigated in order to make keratin a processable material. This review discusses recent developments in the production of thermoplastic keratin blend biocomposites. In particular, the processing and preparation conditions has been discussed, and their strengths and limitations are enumerated and critically evaluated.

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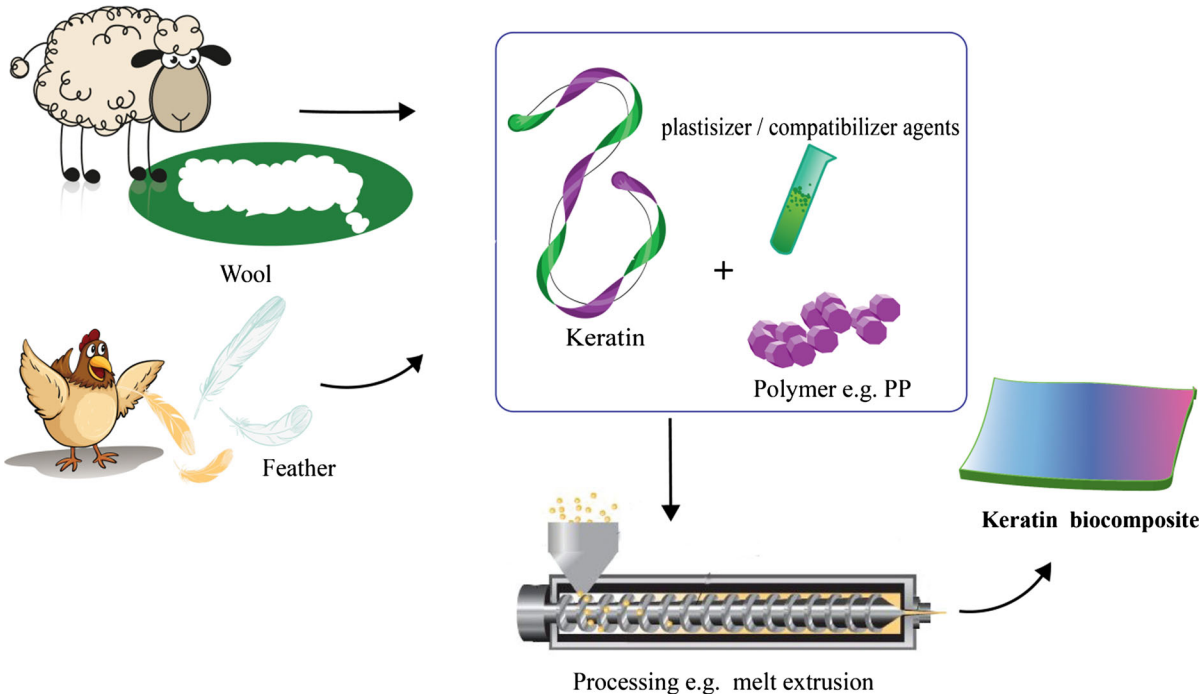
Graphical abstract



Keywords Melt extrusion · Thermoplastic · Biocomposite · Wool · Feather

1 Introduction

There has been an increasing trend in the development of biocomposites using abundant, low-cost and environmentally friendly organic fibres such as wool and feathers. Polymer shrinkage and size reduction do not occur during polymer processing for organic fibres (Barone and Schmidt 2005; Barone et al. 2005) and due to their low density and high strength; the fibre reinforced biocomposites have wide industrial and technical applications. The desired biocomposite should be environmentally degradable through its sensitivity to microbial enzymes and leave no or minimum adverse impact on the environment. Given that organic biodegradable fibres are agricultural by-products and are usually cheap or low cost, one interesting option is to blend organic fibres with inorganic polymers. Therefore, the cost of reinforced polymer production reduces. However, organic fibres are normally sensitive to high temperatures and should normally be processed at temperatures below 200 °C, otherwise, the polymer might start to degrade. On the other hand, a higher temperature is usually required for processing thermoplastic polymers. Therefore, the plastics industry has mainly focused on using non-biodegradable polymers with high thermal stability, such as poly (vinyl chloride) (PVC), polypropylene (PP), polyamide, polystyrene (PS) and polyethylene (PE) (Torres and Cubillas 2005). Nevertheless, organic fillers such as wood fibres and flours have been used to reinforce PE and PP for the production of composites with industrial applications including car panels, doors, furnishings, gardening products etc. (Netravali and Chabba 2003).

1.1 The properties of the protein-based natural fibers

Annually, more than 5 million tons of protein (keratin) based by-products such as waste wool, feathers, horn, and nails are generated from butchery, slaughterhouses, farms and the poultry industry (Shavandi et al. 2017a, b). These natural proteins have some positive characteristics including biodegradability,

biocompatibility and fire retardant capability, however, these by-products are not usually utilised effectively, and due to the high (3–4%) sulphur content of these materials, landfilling or burning can have an adverse impact on the environment (Shavandi and Ali 2019). The application of the protein fibres for reinforcement of polymer composites is one interesting method for processing and development or production of new commodities from these biomasses, and at the same time reduces and recycles these by-products (Conzatti et al. 2013).

2 Current situation

2.1 Polymers used for the biocomposite preparation

Biodegradable polyesters, which normally contain a high fraction of aliphatic ester groups are important synthetic polymers that can be used for the biocomposite production. In addition, polycaprolactone, poly(butylene succinate), polyhydroxy butyrate, poly(butylene succinate-co-adipate), poly(lactic acid), poly(ester amide) and copolyesters based on 1,4-butanediol, adipic and terephthalic acids are some examples of most common polyesters (Table 1) (Avérous and Fringant 2001; Lai et al. 2005; Willett and Felker 2005). These polymers have a wide and diverse range of mechanical and physical properties, which make them comparable to non-biodegradable synthetic polymers such as low and high-density polyethylene (LDPE, HDPE) and poly propylene (PP).

2.2 Natural protein fibers for biocomposite production

There are a limited number of studies dealing with the pre-processing of natural protein fibres, in particular, wool/poultry keratin fibres, prior to incorporation with synthetic polymers for the production of reinforced thermoplastic biocomposites through thermal bonding techniques such as intermixed melt blending. Thermal bonding requires a thermoplastic polymer, which can be a powder, granular, film and web, or a hot melt. In general, this process involves melting the thermoplastic polymer which flows and impregnates or covers the fibres, adheres and bonds to the fibre effectively, then cools and solidifies (Russell and Institute 2007). This review paper aims to review the pre-processing and application of protein-based (keratin) fibres such as wool and feathers for the production of reinforced biocomposites.

3 Techniques for fabrication of wool fibre composites

3.1 Application of untreated wool fibre

Wool fibres have been directly applied for the fabrication of biocomposites without addition of compatibilizer, plasticizer or coupling agents, in one of the early studies, Blicblau et al. (1997) incorporated 21, 40, 52 and 55% wool fibre into polyester resin using a hydraulic pressure of 1.2 MPa for up to 24 h to produce a biocomposite (Table 2). The mechanical properties of the biocomposite increased by increasing the percentage of the wool fibre loading, and a maximum tensile stress of 41.9 MPa was recorded

Table 1 Some of different polypropylene (PP) polymers used in the literature for the preparation of keratin containing composites

Polymer	Density (g/cm^3)	MFI[a] (g/10 min) at 230 °C	References
HP520H	0.9	2	Conzatti et al. (2012)
BI452	–	8	Kim et al. (2014, 2015)
H5300	–	3.5	Kim et al. (2015)
HP 400L	–	5.5	Kim and Bhattacharyya (2016)
HP552R	–	25	Bertini et al. (2013)
PP by Barnet Southern	0.9	20	Huda and Yang (2008)
Recycled PP	0.9	6.0	Amieva et al. (2014)

[a]*MFI* Melt Flow Index

Table 2 Mechanical properties of thermally blended composites comprised keratin or wool

Optimum condition	Tensile modulus (GPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Flexural strength (MPa)	Yield stress (MPa)	References
60% feather + 8% MAPP + PP	2.15	2.17	28.41	56.20	–	Bullions et al. (2004)
20% wool, 4% MAPP + PP	2.7	–	–	–	32	Bertini et al. (2013)
5% feather + PLA	4.2	–	55	–	–	Cheng et al. (2009)
40% wool + polyester	0.576	–	–	–	2.2	Conzatti et al. (2012)
60% wool + PP + MAPP 5%	1.8	–	–	–	15	Conzatti et al. (2013)
20% wool + PP + 5% MAPP	1.7	–	–	–	27	Conzatti et al. (2014)
30% wool + HP400L PP	2.41	–	33.8	–	–	Kim et al. (2014)
30% wool + PP	2.41	–	35	–	–	Kim et al. (2015)
30% wool + PP + 2% MAPP	2.5	2.5	34	55	–	Kim and Bhattacharyya (2016)

for the biocomposite with 55% wool. The authors suggested that the addition of 50% wool results in a six-fold increase in the impact toughness of the biocomposite. Notwithstanding this result, no chemical interaction was reported between the polymers nor an adhesion was observed between the fibres and the polymer matrix (Fig. 1a). The lack of chemical bonding and dispersion along with layer by layer assembly of the fibres before pressing and the long pressing time of 24 h make this biocomposite commercially undesirable.

In another study chopped wool fibres with approximately 0.11 mm length were dry mixed with ground thermoplastics such as polystyrene (PS) and fed into a mini-extruder for melt blending with polymer/wool fibre to produce biocomposites. Fares D. Alsewailem patented a process (US 20160102192 A1 and US 9296155 B2) for preparing the reinforced polymer biocomposites containing 15% wool fibre. Polystyrene and high-density polyethylene (HDPE) was used as an example, and the Izod impact strength increased to above 65 J/m compared to 20 J/m for the pure HDPE composite. Tensile strength also increased to above 20 MPa from 18.75 MPa with the addition of 15% wool fibre. In spite of this improvement in mechanical properties, no information was provided for other mechanical properties of the biocomposite such as modulus, yield strength and the morphological properties of the samples (Table 2). A diverse range of thermoplastics such as PE, PP, PET, PVC, EPDM were also included in the claim of this patent and the inventors suggested that the reported method can be used successfully for all the named thermoplastics without providing supporting information. The patents did not discuss whether pre-treatment was carried out on the wool structure and they provided no evidence regarding the lack of bonding.

3.2 Application of coupling agents and compatibilizers

The mechanical properties of the biocomposite depend largely on the quality of the interfacial adhesion between the fibre and the polymer matrix. Given that most natural fibres such as wool and feathers have hydrophilic surfaces, a composite with weak mechanical properties is expected as a result of the fibre polymer melt blending. To address this issue, a number of compatibilizer or coupling agents such as silane, maleic anhydride, glycidyl methacrylate, maleic anhydride, stearic acid and titanate have been introduced and evaluated to modify the surface and improve polymer fibre adhesion (Abdelmouleh et al. 2007; Conzatti et al. 2014; Liu et al. 2009, 2013).

3.3 Treatment with polyvinyl alcohol (PVA)

In a series of studies, Conzatti et al. prepared different wool containing composites using a melt blending technique and evaluated the physicochemical characteristics of the generated composites (Conzatti et al. 2012, 2013, 2014). In the first study (Conzatti et al. 2012), wool fibres of about 2 cm in length were treated with 3% poly vinyl alcohol (PVA) to increase adhesion with the polyester polymer matrix. Using a melt blending technique at 160 °C, biodegradable

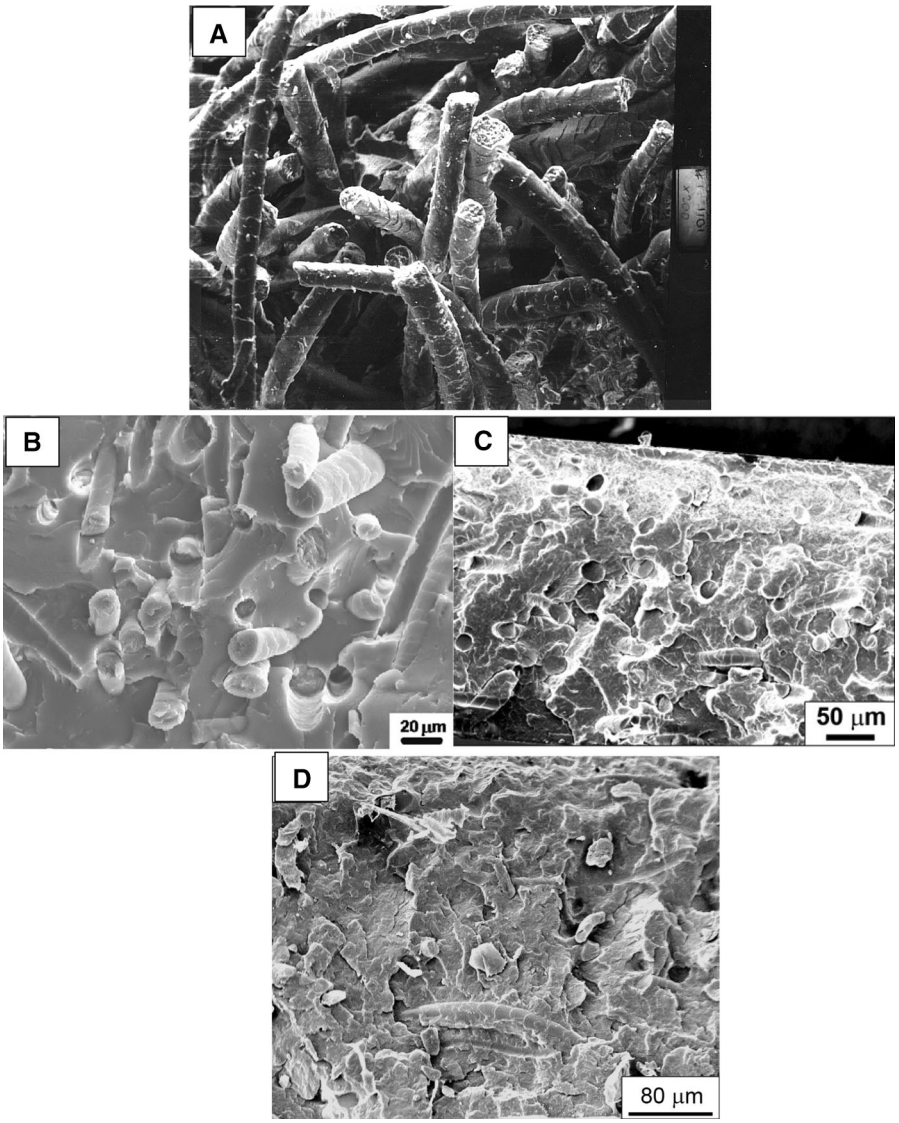


Fig. 1 **a** Scanning electron micrograph of the fracture surface of the 55% wool–polyester biocomposite matrix. Reprinted by permission from Springer (Blicblau et al. 1997). **b** Polyester based composite containing 20% wool fibre (Conzatti et al. 2012). **c** Polypropylene (PP) based composite containing 20% wool fibre and 5% compatibilizer (MAPP) (Conzatti et al. 2013). **d** Polypropylene (PP) based composite containing 20% wool fibre, 5% compatibilizer (MAPP) and 10% silane coupling agent (MPTS) (Conzatti et al. 2014). Reprinted with permission from Elsevier

polyester (BPE) biocomposites with 20, 30 and 40% wool fibre composition were fabricated and then samples formed into sheets with variable thickness. A significantly higher modulus (437 MPa) was observed for the PVA treated samples compared to non-treated fibres (338 MPa). This improvement can be correlated to improve adhesion between the polymer and the fibre due to the PVA treatment (Fig. 1b). PVA acts as a coupling agent, which improves the interfacial interaction between the natural fibre and polyester. In addition, increased wetting of the PVA treated sample can result in the formation of van der Waals bonds, which can justify the observed improved mechanical property. The pre-treatment of fibres with PVA is reported to be beneficial for enhancing the mechanical properties of the biocomposite (Conzatti et al. 2012).

3.4 Incorporation of maleic anhydride grafted polypropylene (MAPP)

In a study, the authors (Conzatti et al. 2013) evaluated the possibility of producing composites containing up to 60% wool fibre. To achieve this goal and to enhance the fibre polypropylene (PP) polymer adhesion and interaction, maleic anhydride grafted polypropylene (MAPP) was used as the compatibilizer (Table 3). The

Table 3 Some of compatibilizer/dispersing and silane coupling agents have used in the literature to bond keratin fibres with other polymers

Compatibilizer/dispersing agent	MFI	Weight ratio (%)	References
MAPP Licocene 6452	Maleic anhydride grafted polyethylene	2, 4, 6	Kim et al. (2014)
COMPOLINE CO/PP	Maleic anhydride grafted polyethylene	5	Bertini et al. (2013)
MVEMA copolymer	Methyl vinyl ether/maleic acid copolymer	10–30	Ghosh et al. (2016)
	50/50 copolymer (molar); Lower molecular weight		
	50/50 copolymer (molar); Higher molecular weight		Ghosh et al. (2016)
Silane coupling agent			
Methacryloxy propyl tri methoxysilane (MPTS)		10	Conzatti et al. (2014)
Methoxy(dimethyl)octadecylsilane (MDOS)		10	Conzatti et al. (2014)

thermal stability of the biocomposites increased by increasing the wool content and this effect was more pronounced with the presence of the compatibilizer. In particular, the authors observed a direct relation between the char yield and the wool fiber content in the composite. Given that the amount of char forms during pyrolysis play an important role in the fire resistant properties of the material, this observation may indicate to flame resistant properties of the wool fiber composite (Conzatti et al. 2013). In addition, the fibres were homogeneously distributed throughout the composite matrix (Fig. 1c). However, fibre polymer matrix interaction was very poor when there was a lack of compatibilizer. Despite the promising results of the improved thermal stability and elastic modulus, the composite strength dropped from around 30 MPa to around 15 MPa by increasing the fibre content from 0 to 60%, and with the addition of compatibilizer, the composite experienced a reduced yield of stress (Conzatti et al. 2013). The critical length of a fibre is the minimum length at which its centre experiences ultimate tensile strength. In the study by Conzatti et al. (2013) the fibres were shorter than their critical length and so they could not exert their reinforcing capability.

Selecting the optimum parameters of mixing/extruding and the type of compatibilizer can improve the final properties of the biocomposite.

In another series of studies performed from 2014 to 2016, Kim and Bhattacharyya (2016), Kim et al. (2014, 2015) focused on the combination of PP with wool fibres for the preparation of fire retardant biocomposites. In their study (Kim et al. 2014), three PP polymers with different melting flow indexes (MFI) of 3.5, 5.5 and 8 g/10 min were used as the matrix media and melt blended with 15, 23 and 30% wool fibre in the presence of 2–6% MAPP Licocene 6452 as the compatibilizer. Tensile moduli of the sample biocomposites increased with the addition of the wool fibres and the compatibilizer, and a maximum increase of more than 55% was reported for PP polymer of HP400L with 5.5 MFI, containing 30% wool and 2% MAPP. In parallel, Mohanty et al. (2004) found that the addition of a high amount (6%) of MAPP had an adverse effect on biocomposite strength. Selection of the right polymer is also of importance, and application of PP with a low MFI of 3.5 (H5300) reduced the strength of the biocomposite.

Therefore, a PP polymer with a medium viscosity was suggested to achieve good dispersion and overall mechanical properties. The importance of the MFI of the polymer on the flexural and tensile properties of the biocomposite has also been reported by other studies (Sallih et al. 2014). Nevertheless, choosing the right polymer viscosity depends on the final application of the biocomposite. Parallel to this, in another study Kim et al. (2015) suggested a PP with a high MFI of 8.0 as the optimum choice for the preparation of fire retardant biocomposites. The PP polymer with a high MFI helped to disperse the aluminum polyphosphate (APP) as a fire retardant agent inside the matrix. A

highly interconnected matrix was observed using the high MFI polymer with the incorporation of 30% wool fibre and 20% APP.

The same research group in two different studies reported a tensile modulus of 2.03–2.5 GPa for PP (H5300) biocomposites containing 30% wool fibre (Kim et al. 2014, 2015). Given that PP (HP400L) with a medium MFI was reported earlier as the polymer of choice with a maximum tensile modulus of 2.41 GPa, it is hard to compare the effectiveness of the type of polymer on the mechanical properties of the biocomposite. Kim et al. (2014) also claimed that the tensile strength of the biocomposites improved with increasing the fibre content, which contradicts studies by Conzatti et al. (2012, 2013).

Both groups of Kim et al. (2014) and Conzatti et al. (2012, 2013) reported higher tensile strength at yield by increasing the addition of wool fibre to the matrix polymer (Conzatti et al. 2012; Kim et al. 2014). In addition, the wool fibre used in Kim et al.'s studies had a diameter of 45 μm which was double the diameter (20 μm) reported for the fibre used by the other group (Conzatti et al. 2012).

The addition of APP increases the tensile modulus and improves the fire-retarding ability of the composite. However, APP is an inorganic phosphate compound which generally reduces and weakens the interaction and adhesion between the wool fibre and polymer at a saturated concentration and also has an adverse effect on the tensile strength of the composite (Lin et al. 2011). To address this issue, in another study, Kim et al. lowered the concentration of APP from 20 to 15%; improved mechanical properties and lower related costs due to the lower incorporation of APP were recorded (Table 1S) (Kim and Bhattacharyya 2016).

3.5 Oxidation and silanization

Coupling agents such as silanes can have an internal plasticizing effect by bridging the interface between the fiber and the polymer matrix (Conzatti et al. 2014). Silanes have been widely used for the preparation of composites containing natural fibers or inorganic fillers (Huda et al. 2008; Metın et al. 2004; Xie et al. 2010). Oxidation also can activate the chemical functionalities of the fiber (-SO_3H, -COOH) required for the silane groups attachment by affecting on the cuticle surface (Conzatti et al. 2014). One research group aimed to modify the surface chemistry of wool fibre using oxidation and silanization to improve the fibre PP polymer interaction (Conzatti et al. 2014). The wool fibers were oxidised using an aqueous solution of hydrogen peroxide, nonylphenol and sodium pyrophosphate and then silanised using 10 wt% relative to the fibres of 3-(methacryloyloxy) propyl] trimethoxysilane (MPTS) and methoxy(dimethyl)octadecylsilane (MDOS). A maximum of 20% wool fibre was incorporated in the polymer matrix and an improved breakage resistance was observed for the samples subjected to both treatments (Fig. 1d).

Fibre oxidation can have a synergistic effect on the silane fibre interaction. After oxidation, more chemical functional groups such as –SO_3H and –COOH are generated on the fibre surface that might be favorable for the interaction of the silane with the fibre. Despite this, fibre treatment had no effect on the biocomposite strength, and identical yield stress was reported for both treated and untreated control samples. In the presence of a coupling agent, the organic fibres and the polymer matrix can bond through strong covalent bonding, while weak van der Waals bonding or similar weak bonds are offered without the coupling agents. Therefore, for a better performing biocomposite, it is better to have covalent bindings (Conzatti et al. 2014). To improve melt spinning, in another study (Ghosh et al. 2017), sheep wool keratin protein treated with 1% of 3-aminopropyl trimethoxy silane and melt extruded with polycaprolactone (PCL). The silane treatment improved the melt spinning properties and enhanced the tensile modulus of the fiber. However, no statistical analysis carried on the data to better evaluate the effect of silane treatment on the mechanical properties of the produced fibre. The author reported a similar melt flow behaviour for the silane treated keratin/PCL and the neat PCL, nevertheless no relevant experimental data was provided to support this claim, and no information was provided on the possible effect of keratin treatment with different concentrations of silanes on the homogeneity and spinning behaviour of the keratin/PCL.

3.6 Effect of plastisizers

The addition of plasticisers can help achieve a uniform distribution of the fibre within the polymer matrix and prevent the agglomeration of the fibre materials.

Glycerol was used as the plasticizer by Xu et al. (2007) for the preparation of a biocomposite using 5–60% fine wool powder with an average particle size of 1.7 mm. The mechanical properties of the composites decreased in all tested conditions and by increasing the fibre content, the breaking energy, tensile strength and modulus of the composite decreased. Given that the fine wool powder was not in the nano-size scale, it, therefore, did not merge and integrate well with the polymer matrix. Consequently, the addition of the fibre resulted in cavity formations in the biocomposite sheet. The authors also used a high concentration of glycerol (30%) but without the addition of a coupling agent or a pre-treatment of the wool; therefore, the produced biocomposites had weak mechanical properties.

4 Techniques for fabrication of feather biocomposites

4.1 Application of untreated feather fibre

Feathers are another important source of keratin protein, which is abundantly available. This biological by-product can be utilised for the preparation of various thermoplastic biocomposites and could, therefore, improve economic returns for the poultry industry. Feather keratin is comprised of small protein molecules with a molecular weight of 10–30 kDa. Feather keratin, like wool, is high in cysteine and has hydrophobic amino acid residues which form the beta sheet conformation (Poole et al. 2009). Keratin has extensive internal bonding which makes it very stable thermally and mechanically (Poole et al. 2009). In addition, being cheap and naturally abundant makes feather keratin an ideal material for the production of biodegradable thermoplastic biocomposites for diverse applications.

Up to 50% feather fibres with a length of 2 mm and smaller were incorporated into low and high-density PE (LDPE and HDPE) by Barone et al. (2005), Barone and Schmidt (2005) (Fig. 2a–c). In these two studies, increasing the fibre aspect ratio and feather fibre loading up to 40% resulted in the modulus and yield stress increasing while the yield strain decreased. Nevertheless, the peak stress and strain decreased. Similar results have been reported for the addition of feather fibre into PP (Bullions et al. 2004). Using HDPE, the authors suggested a processing temperature of 205 °C at 75 RPM for up to 10 min as the optimum extrusion conditions.

High or low-density Polyethylene (PE) with different crystallinity was used in another study by Barone (2005) to prepare biocomposites with 20% feather keratin. It was reported that low-density PE with a crystallinity index of less than 0.5 could reinforce and adhere the keratin fibre. However, there was a weak adhesion between high-density PE with a crystallinity index of 0.5 and the keratin fibre. Given the better interaction of the low-density polymers (e.g. LDPE) with the fibre, these biocomposites showed significantly higher mechanical properties compared to biocomposites made with the high-density polymer (e.g. HDPE). The authors indicated that keratin fibre that comprises 60% hydrophobic and 40% hydrophilic amino acids could be compatible with the hydrophobic PE.

During their lifetime composite structure may be exposed to various effects such as weathering, heat, etc. which lead to their degradation and eventually suppress their mechanical properties. Therefore it is important to have knowledge of biocomposites resistant to weathering conditions. In a study, up to 10% of the LDPE polymer replaced with feather fibre and the melt extruded composite subjected to the aging process. After 500 h of weathering at 40 °C with a relative humidity of 60% and exposure to artificial light, a significantly higher content of carbonyl and vinyl groups detected in the samples indicating to the surface degradation of the composites. However, the composite strength and flexibility were not compromised and the author suggested feather fibre as a suitable candidate to partially replace synthetic polymers. It is, however, worth nothing that the weathering studies need to be carried out for the composite with higher content of the fibre and at the various condition to better reflect the suitability of the feather as a filler in these composites. In addition, other parameters such as aesthetic aspects may be affected by the surface oxidation/surface micro cracks which may suppress the successful production and application of this composite (Spiridon et al. 2012). It is important to have good interaction between fiber and the polymer to achieve a good fiber reinforcement. Therefore different additives including coupling agents or compatibilizers have been used to enhance the chemical

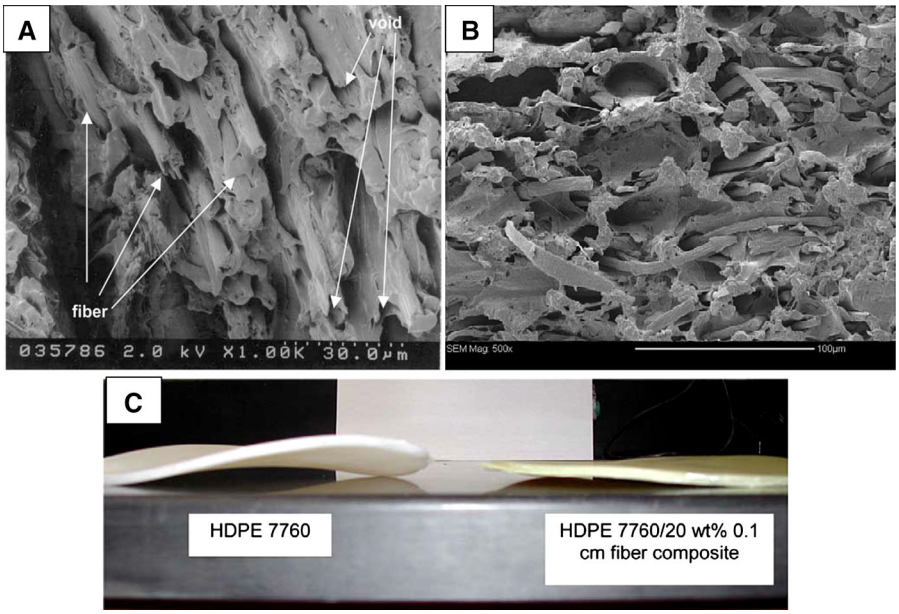


Fig. 2 **a** Low-density polyethylene (PP) and **b** polyethylene (PE) based composite containing 40 wt% 0.1 cm keratin feather fibre. **c** High-density polyethylene (HDPE) film. Pure HDPE (left) and 20% fibre containing composite (right) (Barone and Schmidt 2005; Barone et al. 2005)

compatibility between these two hydrophobic and hydrophilic phases of the keratin fibre.

4.2 Stearic acid and isopropyl tri (dioctylpyrophosphate) titanate

Stearic acid is also a good example of fibre/polymer surface modifier. It has long hydrocarbon chains, which makes it compatible with polypropylene. Stearic acid can also react with the hydroxyl and amine groups present on the surface of keratin fibres and form ester and amide linkages. Therefore, stearic acid can be a potential modifier to improve interfacial adhesion between the fibres and polymer resin. The effect of stearic acid as a surface modifier was investigated by Liu et al. (2013), and efficient improvement in the dispersion of keratin fibre powder in a polypropylene matrix was observed and reported. In addition, the stearic-modified samples showed higher tensile strength and elongation at break. Isopropyl tri (dioctylpyrophosphate) titanate (NDZ-201), similar to stearic acid, can react with hydroxyl, carboxyl and amino groups on the keratin fibre and form a Ti–O bond. It is also compatible with PP due to its long chain hydroxyl groups. Given these properties, NDZ-201 was used for modification of down feather whiskers. The modified feather whiskers were compounded with PP in a twin-screw extruder to generate thermoplastic biocomposite samples. Uniform whisker dispersion was observed in the biocomposite samples, which had higher mechanical properties, and in particular, higher tensile strength and Young's modulus, compared to the biocomposite produced with non-modified whiskers.

Using FT-IR analysis it was inferred that NDZ-201 formed a molecular layer on the feather short fibers or whiskers surface and esterification occurred between the fibre and the PP polymer which resulted in a successful grafting. This grafting improved the thermal stability of the biocomposite as well as increasing the interfacial adhesion between the fibre and the PP polymer. The better thermal stability of the biocomposite could also be due to the presence of a large number of phosphate groups in the macromolecular backbone of NDZ-20 (Liu et al. 2013).

4.3 Effect of ε-caprolactam

The possible effect of coupling agent, ε-caprolactam on tensile properties, thermal degradation, morphology and swelling behavior of recycled high-density polyethylene–chicken feather fiber composites (r-

HDPE/CFF) were studied by Supri et al. (2013). The addition of ε-caprolactam increased the interfacial adhesion and the tensile strength increased as the fiber loading increased up to 7.5%, and a higher tensile strength reported for the composite with ε-caprolactam compared to the control, nevertheless this possible positive effect of ε-caprolactam was not supported by statistical evaluation and in addition incorporation of ε-caprolactam had a negative impact on the elongation at break by increasing the stiffness of the composites.

4.4 Application of maleic anhydride (MA)

Maleic anhydride (MA) grafted polypropylene (PP) or polyethylene (PE) are examples of two widely used additives to enhance the mechanical properties of PP- or PE-based fibre reinforced biocomposites (Colom et al. 2003; Joseph et al. 2003; Wambua et al. 2003). The addition of MA with the concentration of 0.1–2% can generally increase ultimate strength (Rana et al. 2003). Hydrogen bonding between the MA-PP along with covalent bonds between fibre hydroxyl groups and carbonyl groups on the MA are responsible for interactions between MA-PP and the natural fibre (Barone and Gregoire 2006).

By incorporating MA to PP, the surface of the natural fibre serves as the nucleation sites for polymer crystal formation. These crystals are different from the normal polymer crystals in the bulk. This trans-crystalline phase provides a bridge between the fibre and the polymer.

The tensile properties of the feather fibre/PP biocomposite did not improve significantly with the addition of MA-PP, nevertheless, in the absence of MA, PP composites showed lower breaking stress. MA-PP with a concentration of less than 4% was reported as ideal for improving the breaking stress, melting point and crystallinity of the biocomposite. A further increase in MA and PP concentration (> 4%) was reported as detrimental to the biocomposite structure (Barone and Gregoire 2006).

In spite of this, in another study, 8 wt% of MA-PP was reported as the optimum concentration for the preparation of feather fibre reinforced biocomposites when up to 8% feathers were added to the polymer matrix. This discrepancy in optimum MA-PP concentrations can be due to the rate of cooling, the percentage of incorporated natural fibre, type and properties of tested polypropylene and also the type and properties of the MA-PP system used.

4.5 Application of methacrylate monomers (MMA)

In a study by Martínez-Hernández et al. (2007), the chicken keratin reinforced biocomposite prepared by polymerisation of methyl methacrylate monomers (MMA) initiated with 2,2-azobis-isobutyronitrile (AIBN), and composite sheets were produced after the mixture was transferred to a mould. Despite reports that the incorporation of keratin was beneficial to the mechanical properties of the biocomposite, only the biocomposites containing 1–2% keratin fibre showed higher storage modulus compared to non-reinforced composites.

This result hints that the high fibre concentration might interfere with the polymerisation of the MMA monomers; therefore incorporation of higher fibre content into the polymer matrix to produce a good composite material is challenging. It is demonstrated that incorporation of a very low amount (volume) of the natural fibre (1–2%) limits this technique. Hence, this method might not be an ideal option when the aim is valorisation of abundant natural by-products such as wool and feathers.

4.6 Application of feather quill

The feather industry in the United States alone produces more than three billion pounds of feather annually. Part of this is converted to animal feed additives (Huda and Yang 2008). Feather comprises of three different parts: quill, pennaceous and plumulaceous fibres, where the quill comprises 50% of the total weight of the feather. The quill is primarily made of keratin protein with a beta-sheet structure and a lower amount of alpha keratin with a denaturing temperature of 230 °C (Huda and Yang 2008). Despite more than half of the feather consisting of the quill, most of the studies regarding the application of the feather for biocomposite production have focused on using feather fibres but not the quill (Barone and Schmidt 2005; Barone et al. 2005; Bullions et al. 2004, 2006).

With this in mind, Huda et al. incorporated milled quill into the PP matrix using a hot press molding. All the measured mechanical properties including tensile

strength, modulus, impact resistance, and flexural strength increased by increasing the quill concentration up to 30% (Huda and Yang 2008).

The length of industrially processed chicken fibres is normally below 15 mm, while the barbs of a native feather can be around 30 mm (Huda and Yang 2008). In compared to cellulose-based fibers such as jute fiber, feather quill is largely composed of hydrophobic alkyl groups which may justify its better physical interaction with synthetic polymers such as PP which has no OH group and is hydrophobic (Huda and Yang 2008). These longer length fibres can be beneficial for improving the mechanical properties of the biocomposite. Notwithstanding, it is difficult to fabricate a well-mixed biocomposite with good structural properties using long length fibres.

4.7 Biocomposite reinforced with feather powder

Nevertheless, PP biocomposites containing up to 60% whole chicken feathers were fabricated using a compression molding technique by Reddy and Yang (2010). Higher mechanical properties such as flexural, tensile strength and modulus were reported for the biocomposites containing whole feathers compared to biocomposites that had powdered quill. Furthermore, the biocomposites with whole feathers recorded the lowest modulus of elasticity, probably due to the non-homogeneous structure of the biocomposite. In addition, an increasing sound absorption trend was observed for the biocomposites with increasing amounts of the fibre. In this regard, whole chicken feather fibre might be faster and easier filler material for fabricating biocomposites when high mechanical properties and elasticity, in particular, is not essential. In a subsequent study, Reddy et al. (2014) replaced the PP with the feather powder as the matrix material. Jute fibres with feather powder and 5% glycerol were mixed and compress molded at 205–215 °C. Despite the higher tensile and flexural properties of the biocomposites compared to the control PP composite, the fabricated biocomposites suffered from poor mechanical properties under humid conditions with more than 50% reduction in mechanical properties recorded at high humidity. The high hydrophilicity of both the jute and feather fibres might be the main reason for the poor mechanical performance of the biocomposite.

4.8 Feather reinforced biocomposites with electrical resistance

The possibility of fabricating keratin reinforced biocomposites with high electrical resistance and a low dielectric constant for application in the electronic device industry was first evaluated by a research group from Delaware University (Hong and Wool 2005; Zhan and Wool 2010; Zhan et al. 2011). Chicken feather reinforced epoxy biocomposites were made through a moulding and hot pressing process. Biocomposites with up to 45% chicken fibre showed a low dielectric constant of 3.6–4.2, similar to those of commercially printed circuit board materials (Hong and Wool 2005; Zhan et al. 2011).

4.9 Incorporation of the feather into the natural polymer

Fibre reinforced polyolefin synthetic polymers such as PP and PE are not yet a 100% natural biocomposite (Mohanty et al. 2002). Therefore, after a number of trials on the incorporation of feather in PP by Barone (2005), Barone and Gregoire (2006), Barone and Schmidt (2005), Barone et al. (2005, 2006), Mohanty et al. (2002). Barone (2009) investigated the possibility of fabricating a 100% natural fibre-based biocomposite using keratin fibre combined with lignocellulose fibres such as wheat straw, corn stalk, kenaf, hemp etc. A hot pressing technique (i.e., compression moulding technique) was used to make keratin fibre at a weight ratio of up to 40%. No strong bonding formed and only moderate hydrogen bonding was observed between the keratin fibre and lignocellulosic materials.

Incorporation of feather fibres into polylactic acid (PLA) polymer was studied by Cheng et al. (2009). Thermoplastic biocomposites containing PLA and variable feather concentrations of 2–10% were synthesised and a decreasing trend for tensile strength was observed by increasing the feather content. However, this decrease was not substantial (less than 10 MPa) and the biocomposite has been suggested for low load-bearing applications. In addition, tensile modulus and elongation at break (EAB) values were higher than the PLA composite for all fibre concentrations; maximum tensile value of 4.2 GPa was reported for the samples with 5% feather fibre. The fibres might act as a bridging agent which increases the tensile modulus

and EAB. The highest thermal stability and best dispensability in the PLA matrix was also reported for the samples with 5% feather content. Using the natural polymer polyhydroxyalkanoates (PHAs) for melt compounding with keratin isolated from feather fiber, Pardo-Ibáñez et al. (2014), observed enhanced barrier properties of the composites. The composites with 1 wt% of keratin showed a 50% reduction in water, limonen and oxygen permeability making it suitable for food packaging. In addition, a 30% increase on the elastic modulus was observed in the composite containing 10% keratin fibers in compared to the pristine polymer. Nevertheless, the composite had poor optical properties. In most of the studies mentioned earlier, the keratin fibre was incorporated into the polymer matrix in its natural form without copolymerisation with other monomers.

4.10 Application of deconstructed fiber for biocomposite preparation

Using whole wool fibre for the preparation of thermoplastic biocomposite without pre-processing the fibre can reduce the cost of the final composite products. However, deconstructing the wool structure to isolate the keratin protein for incorporation into the biocomposite has been also investigated by some research groups (Dou et al. 2016; Liebeck et al. 2017). Nevertheless, the process of the fiber deconstruction for breaking down the compact fiber structure and isolation of keratin can be expensive, not commercially interesting and might have a negative impact on the environment depending on the selected processing method. The conventional methods for extraction of keratin including reduction using chemicals such as mercaptoethanol, urea or sulphitolysis using disodium hydrogen sulphate, or oxidation using oxidising agents such as hydrogen peroxide or acetic acid (Shavandi et al. 2016), are neither commercially, nor environmentally interesting.

In this regard, Bertini et al. (2013) used a green hot critical water extraction method for extracting keratin from the wool fibre. The obtained keratin was melt extruded with PP and a 5% MAPP was also used to further improve the distribution of the keratin in the PP polymer matrix. Improved mechanical properties, including elastic modulus, were observed for the sample containing 5% keratin powder. This improvement could be due to the effect of keratin improving the PP crystallisation rate. In a follow-up, extended study (Canetti et al. 2013), the effect of extracted keratin on the crystalline structure, morphology, melting properties and kinetics of crystallisation was evaluated by the authors. Keratin was homogeneously distributed within the composite structure and did not interfere with the spherulitic growth of polypropylene crystals (Fig. 3a). In fact, keratin favoured the PP crystallisation. It was also observed that the keratin particles were moved out of the inter-lamellar regions of PP to the intra/inter spherulitic regions. The presence of lipids in the cuticle layer of the wool fibre (outer layer) makes wool hydrophobic, reduces the surface energy of the fibre, and results in weak bonding properties of the fibre and the thermoplastic polymers.

4.11 Other methods of biocomposite preparation

Disulphide bonds along with hydrogen and ionic bonds give keratin a complex, cross-linked structure, which makes it nonsoluble in most of the usually available solvents. Therefore, the wet blending of these fibres with other polymers is not a straightforward process. However, keratin can be extracted and converted to more processable materials. There are a number of methods for keratin extraction, such as reduction, sulfitolysis, oxidation, ionic liquids, etc. (Aluigi et al. 2007; Blackburn and Lee 1956; Idris et al. 2013; Kakkar et al. 2014; Katoh et al. 2004; Poole et al. 2011). A keratin/polyethylene oxide (PEO) blend containing up to 7% keratin was prepared by Aluigi et al. (2008b) for electrospinning. The presence of keratin in the PEO matrix at high concentrations of 7% was not desirable for the electrospinning process due to the low viscosity of the solution and bead formation during the process. The poor mechanical properties of the produced fibres and low water stability of the keratin/PEO mixture were other limiting factors in this process. Notwithstanding, the biocomposite was reported as a potentially useful material for the preparation of air filters for removal of volatile organic compounds (Aluigi et al. 2008b).

In another study, Fan et al. tried to address the poor mechanical properties of the keratin/PEO fibre and improve the electrospinning ability keratin/PEO by cross-linking the material. Keratin/PEO with the ratio of 90/10 (w/w) was prepared and cross-linked with the

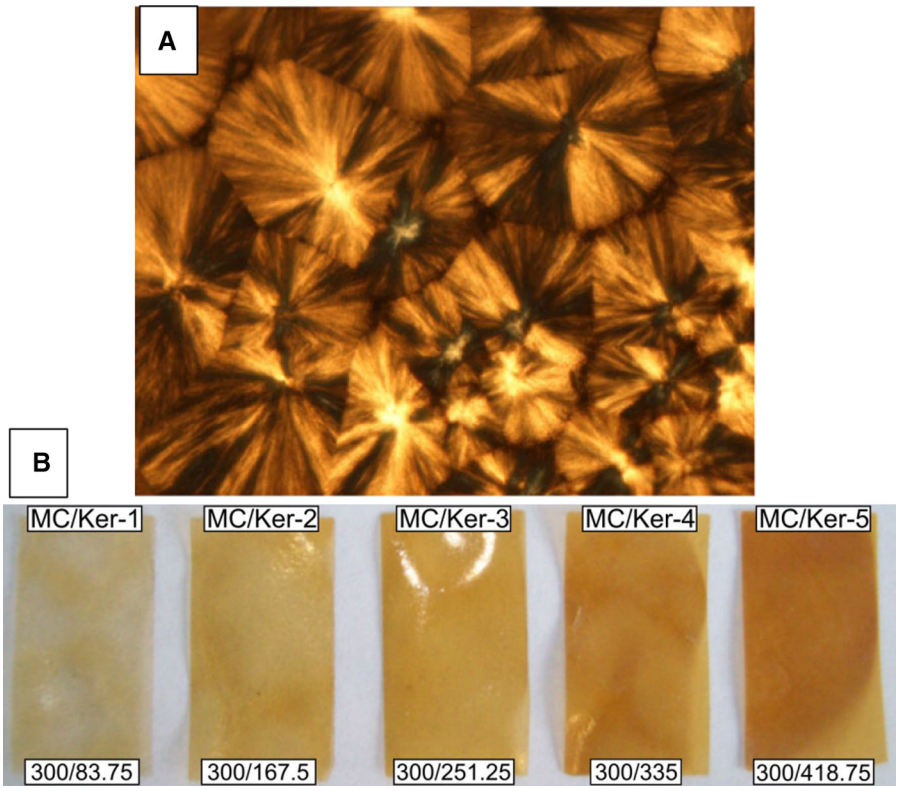


Fig. 3 **a** Polarising optical photomicrographs of Polypropylene/keratin 80/20: after complete crystallisation at Tc = 131 °C (Canetti et al. 2013). **b** Biocomposite films produced from hot critical water keratin hydrolysate (Ker) and methyl cellulose (MC) with different ratios. 25 µl of Glycerol was used as plasticizer in all of the formulations. Young's modulus and offset yield strength decrease with increasing the ratio of keratin suggesting that keratin with low molecular weight acted similar to a plastisizer in the polymer network (Liebeck et al. 2017)

addition of ethylene glycol diglycidyl ether (EGDE). An improvement in the electrospinning processability of the blend was observed which could be due to an increase in the molecular weight of the keratin after cross-linking by EGDE. This cross-linked keratin also showed high crystallinity and thermal stability compared to non-cross-linked keratin biocomposites. The prepared biocomposite has been suggested for cell culture and other tissue engineering applications.

In continuing to improve the mechanical properties of the keratin/PEO biocomposite, Grkovic et al. reported their study on reinforced keratin/PEO biocomposite with graphene oxide using ultrasonication techniques. The biocomposite with the keratin/PEO ratio of 90/10 (w/w) was prepared by a solvent casting method. The addition of as low as 0.3% wt. of graphene to the polymer matrix resulted in a 92% increase of the biocomposite's storage modulus. Despite the increase in the mechanical properties of the biocomposite and its potential applications for high-performance materials, scaling up the process and ease of manufacturing are challenges that still need to be addressed (Grkovic et al. 2015).

In a later study by Aluigi et al., the possibility of blending keratin with nylon (PA6) was investigated. Using a solution blending method, the authors incorporated 50 to 90% keratin into the PA6 matrices; the copper (II) adsorption capability of the fibres was evaluated. A positive correlation was observed between the concentration of keratin and the copper adsorption capacity of the fibre, where the maximum adsorption of 103.5 (mg/g) was reported for the 90% keratin composites. This reported adsorption capacity is higher than the 50 mg/g that was reported for the commercially available active Carbone for ion pollution removal (Aluigi et al. 2011).

In addition to synthetic polymers of PEO and polyamide, keratin has also been incorporated into

various naturally biodegradable polymers such as PLLA (Li et al. 2009), silk (Baek et al. 2007; Rajkumar et al. 2013), cellulose (Aluigi et al. 2008a) and alginate (Gupta and Nayak 2015). Cellulose composites with 20% wool keratin extracted from cortical cells were reported as films with improved mechanical properties with biodegradation ability which can be used for packaging or various textile fibres (Aluigi et al. 2008a). Similarly, alginate composites with 20% keratin showed maximum tensile properties, and keratin was miscible within the alginate matrix (Gupta and Nayak 2015) and cellulose (Aluigi et al. 2008a). Cellulose composites with 20% keratin cortical cells were reported as films with improved mechanical properties with biodegradation abilities which can be used for the packaging or various textile fibres (Aluigi et al. 2008a). Similarly, alginate composites with 20% keratin showed maximum tensile properties and keratin was miscible within the alginate matrix (Gupta and Nayak 2015). In another work, surface-functionalized cellulose nanocrystals (CNC) incorporated into the keratin structure. For this purpose dialdehyde groups were introduced onto the CNC surface, making it a reinforcing and crosslinking agent. Formation of percolating nanofiller network in the matrix of keratin and enhanced interfacial adhesion were reported responsible for reinforcing the effect of the biocomposite. The suggested reinforcing and crosslinking approach using CNC may lead to the development of high-performance keratin composites for diverse applications in the field of biomaterials such as tissue engineering (Song et al. 2017).

As mentioned earlier, keratin can be extracted through a green environmentally method based on the hot critical water. The keratin extracted using hot critical water is free from the hazardous solvents and is environmentally safe techniques; however, this extraction method results in short keratin chains with 10–20 (Zhang et al. 2012) amino acids which result in final composites with inferior mechanical properties. To address this, Liebeck et al. (2017) fabricated composite membranes from a mixture of feather keratin and methylcellulose. The introduction of polypeptides into the cellulose chains resulted in a specific fluctuation in the three-dimensional structure mimicking the protein structure. The films were flexible and free from visible defects which suggested combining the properties of both protein and polysaccharides (Fig. 3b). In particular, the addition of keratin made the films flexible and less brittle in compared to pure methylcellulose films.

In the case of keratin/silk biocomposite, a 50/50 (w/w) blending ratio was reported as optimum in terms of mechanical properties. The possibility of incorporating higher concentrations of keratin into the silk could be due to the physical interaction between silk and the keratin molecules. The low stability of the keratin solution for electrospinning, its brittleness and the bead formation during electrospinning of the keratin solution was addressed by incorporating up to 50% silk in the keratin solution by Baek et al. (2007). Given the good stability of the silk keratin solution and its ease of electrospinning, the authors reported a keratin/silk composite with good mechanical properties which were suggested for the adsorption of toxic metals from polluted water streams. However, clear evidence of the potential of keratin for various textile, packaging, tissue engineering, and adsorption capabilities, the yield and cost of keratin extraction remains unresolved. Additionally, the complexity of the chemical process and the possible impact of the extraction process and its waste stream on the environment has also not been fully addressed yet. In most of the above-mentioned studies the keratin fibrous material was segregated which is costly and time-consuming, with this regard there are studies that considered a solution casting method (Gokce et al. 2017; Pourjavaheri et al. 2018). In a recent work, Pourjavaheri et al. (2018) evaluated a solvent dispersion approach to develop thermoplastic polyurethane. The composite fabricated by adding up to 70% of ground feather fiber to TPU-polyether dissolved in Tetrahydrofuran (THF) solution followed by evaporation. The addition of feather powder improved the elastic modulus of the composite; however, the loss tangent and recovery strain decreased and the addition of 20% of the feather powder suggested as the optimum volume fraction by the author. It is worth noting that addition of the powder decreased the recovery strain and the glass transition temperature of the composite, which was probably due to hydrogen bonding between the fibre and urethane group and consequently restraining the volumetric relation of the polymer. This reduction in the glass transition temperature may affect and limit the final application of the feather reinforced polyurethane composite (Pourjavaheri et al. 2018).

5 Conclusion

The potential use of natural fibres, in particular, wool and feather fibre, for the production of thermoplastic biocomposites through intermixed blending and melt processing have been discussed in this review paper. A large number of studies has been performed on the development of natural fibre biocomposites, however, the manufacturing of these biocomposites has not yet been practiced at an industrial scale. Further research is required to improve the properties of the final product, such as the low strength of the biocomposites and poor adhesion between the protein fibre and polymer matrix. In addition the biocomposites suffer from poor optical properties; nevertheless, the outlook of the application of various crosslinkers, compatibilizers, and coupling agents is likely to be promising. Wool, feather and general keratin-based by-products can be successfully incorporated in the production of reinforced biocomposites. Thus it is essential to develop processing strategies including physical or chemical pre-treatments of fibres to produce suitable and functional biocomposites. The produced biocomposites consisting of modified fibres or keratin are expected to have a certain degree of degradability and low-density with essential flexibility towards their applications. The hydrophilic properties of these biocomposites can also be advantageous in the production of reconstituted hydrophilic fibres, breathable plastics or fabrication of added value biomaterials for biomedical applications.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Abdelmouleh M, Boufi S, Belgacem MN, Dufresne A (2007) Short natural-fibre reinforced polyethylene and natural rubber composites: effect of silane coupling agents and fibres loading. Compos Sci Technol 67:1627–1639. https://doi.org/10.1016/j.compscitech.2006.07.003

Aluigi A, Zoccola M, Vineis C, Tonin C, Ferrero F, Canetti M (2007) Study on the structure and properties of wool keratin regenerated from formic acid. Int J Biol Macromol 41:266–273. https://doi.org/10.1016/j.ijbiomac.2007.03.002

Aluigi A, Vineis C, Ceria A, Tonin C (2008a) Composite biomaterials from fibre wastes: characterization of wool–cellulose acetate blends. Compos Part A Appl Sci Manuf 39:126–132. https://doi.org/10.1016/j.compositesa.2007.08.022

Aluigi A, Vineis C, Varesano A, Mazzuchetti G, Ferrero F, Tonin C (2008b) Structure and properties of keratin/PEO blend nanofibres. Eur Polym J 44:2465–2475. https://doi.org/10.1016/j.eurpolymj.2008.06.004

Aluigi A, Tonetti C, Vineis C, Tonin C, Mazzuchetti G (2011) Adsorption of copper(II) ions by keratin/PA6 blend nanofibres. Eur Polym J 47:1756–1764. https://doi.org/10.1016/j.eurpolymj.2011.06.009

Amieva EJ-C, Velasco-Santos C, Martínez-Hernández A, Rivera-Armenta J, Mendoza-Martínez A, Castaño V (2014) Composites from chicken feathers quill and recycled polypropylene. J Compos Mater. https://doi.org/10.1177/0021998313518359

Avérous L, Fringant C (2001) Association between plasticized starch and polyesters: processing and performances of injected biodegradable systems. Polym Eng Sci 41:727–734. https://doi.org/10.1002/pen.10768

Baek DH, Ki CS, Um IC, Park YH (2007) Metal ion adsorbability of electrospun wool keratose/silk fibroin blend nanofiber mats. Fiber Polym 8:271–277. https://doi.org/10.1007/BF02877269

Barone JR (2005) Polyethylene/keratin fiber composites with varying polyethylene crystallinity. Compos Part A Appl Sci Manuf 36:1518–1524. https://doi.org/10.1016/j.compositesa.2005.03.006

Barone JR (2009) Lignocellulosic fiber-reinforced keratin polymer composites. J Polym Environ 17:143–151. https://doi.org/10.1007/s10924-009-0131-1

Barone JR, Gregoire NT (2006) Characterisation of fibre–polymer interactions and transcrystallinity in short keratin fibre–polypropylene composites. Plast Rubber Compos 35:287–293. https://doi.org/10.1179/174328906X146478

Barone JR, Schmidt WF (2005) Polyethylene reinforced with keratin fibers obtained from chicken feathers. Compos Sci Technol 65:173–181. https://doi.org/10.1016/j.compscitech.2004.06.011

Barone JR, Schmidt WF, Liebner CFE (2005) Compounding and molding of polyethylene composites reinforced with keratin feather fiber. Compos Sci Technol 65:683–692. https://doi.org/10.1016/j.compscitech.2004.09.030

Barone JR, Schmidt WF, Gregoire NT (2006) Extrusion of feather keratin. J Appl Polym Sci 100:1432–1442. https://doi.org/10.1002/app.23501

Bertini F, Canetti M, Patrucco A, Zoccola M (2013) Wool keratin-polypropylene composites: properties and thermal degradation. Polym Degrad Stab 98:980–987. https://doi.org/10.1016/j.polymdegradstab.2013.02.011

Blackburn S, Lee GR (1956) The reaction of wool keratin with alkali. Biochem Biophys Acta 19:505–512. https://doi.org/10.1016/0006-3002(56)90474-7

Blicblau AS, Coutts RSP, Sims A (1997) Novel composites utilizing raw wool and polyester resin. J Mater Sci Lett 16:1417–1419. https://doi.org/10.1023/A:1018517512425

Bullions TA, Gillespie RA, Price-O'Brien J, Loos AC (2004) The effect of maleic anhydride modified polypropylene on the mechanical properties of feather fiber, kraft pulp, polypropylene composites. J Appl Polym Sci 92:3771–3783. https://doi.org/10.1002/app.20369

Bullions TA, Hoffman D, Gillespie RA, Price-O'Brien J, Loos AC (2006) Contributions of feather fibers and various cellulose fibers to the mechanical properties of polypropylene matrix composites. Compos Sci Technol 66:102–114. https://doi.org/10.1016/j.compscitech.2005.03.017

Canetti M, Cacciamani A, Bertini F (2013) Structural characterization and thermal behaviour of wool keratin hydrolizates-polypropylene composites. J Polym Res 20:181. https://doi.org/10.1007/s10965-013-0181-x

Cheng S, K-t Lau, Liu T, Zhao Y, Lam P-M, Yin Y (2009) Mechanical and thermal properties of chicken feather fiber/PLA green composites. Compos Part B Eng 40:650–654. https://doi.org/10.1016/j.compositesb.2009.04.011

Colom X, Carrasco F, Pagès P, Cañavate J (2003) Effects of different treatments on the interface of HDPE/lignocellulosic fiber composites. Compos Sci Technol 63:161–169. https://doi.org/10.1016/S0266-3538(02)00248-8

Conzatti L, Giunco F, Stagnaro P, Capobianco M, Castellano M, Marsano E (2012) Polyester-based biocomposites containing wool fibres. Compos Part A Appl Sci Manuf 43:1113–1119. https://doi.org/10.1016/j.compositesa.2012.02.019

Conzatti L, Giunco F, Stagnaro P, Patrucco A, Marano C, Rink M, Marsano E (2013) Composites based on polypropylene and short wool fibres. Compos Part A Appl Sci Manuf 47:165–171. https://doi.org/10.1016/j.compositesa.2013.01.002

Conzatti L et al (2014) Wool fibres functionalised with a silane-based coupling agent for reinforced polypropylene composites. Compos Part A Appl Sci Manuf 61:51–59. https://doi.org/10.1016/j.compositesa.2014.02.005

Dou Y, Zhang B, He M, Yin G, Cui Y (2016) The structure, tensile properties and water resistance of hydrolyzed feather keratin-based bioplastics. Chin J Chem Eng 24:415–420. https://doi.org/10.1016/j.cjche.2015.11.007

Ghosh A, Carran RS, Grosvenor AJ, Deb-Choudhury S, Haines SR, Dyer JM (2016) Feather meal-based thermoplastics: Methyl vinyl ether/maleic anhydride copolymer improves material properties. Fiber Polym 17(1): 9–14. https://doi.org/10.1007/s12221-016-5291-8

Ghosh A, Ali A, Collie SR (2017) Effect of wool keratin on mechanical and morphological characteristics of polycaprolactone suture fibre. JTE 63:1–4. https://doi.org/10.4188/jte.63.1

Gokce O, Kasap M, Akpinar G, Ozkoc G (2017) Preparation, characterization, and in vitro evaluation of chicken feather fiber–thermoplastic polyurethane composites. J Appl Polym Sci 134:45338. https://doi.org/10.1002/app.45338

Grkovic M, Stojanovic DB, Kojovic A, Strnad S, Kreze T, Aleksic R, Uskokovic PS (2015) Keratin-polyethylene oxide bio-nanocomposites reinforced with ultrasonically functionalized graphene. RSC Adv 5:91280–91287. https://doi.org/10.1039/C5RA12402F

Gupta P, Nayak KK (2015) Compatibility study of alginate/keratin blend for biopolymer development. J Appl Biomater Func 13:e332–e339. https://doi.org/10.5301/jabfm.5000242

Hong CK, Wool RP (2005) Development of a bio-based composite material from soybean oil and keratin fibers. J Appl Polym Sci 95:1524–1538. https://doi.org/10.1002/app.21044

Huda S, Yang Y (2008) Composites from ground chicken quill and polypropylene. Compos Sci Technol 68:790–798. https://doi.org/10.1016/j.compscitech.2007.08.015

Huda MS, Drzal LT, Mohanty AK, Misra M (2008) Effect of chemical modifications of the pineapple leaf fiber surfaces on the interfacial and mechanical properties of laminated biocomposites. Compos Interfaces 15:169–191. https://doi.org/10.1163/156855408783810920

Idris A, Vijayaraghavan R, Rana UA, Fredericks D, Patti AF, MacFarlane DR (2013) Dissolution of feather keratin in ionic liquids. Green Chem 15:525–534. https://doi.org/10.1039/C2GC36556A

Joseph PV, Joseph K, Thomas S, Pillai CKS, Prasad VS, Groeninckx G, Sarkissova M (2003) The thermal and crystallisation studies of short sisal fibre reinforced polypropylene composites. Compos Part A Appl Sci Manuf 34:253–266. https://doi.org/10.1016/S1359-835X(02)00185-9

Kakkar P, Madhan B, Shanmugam G (2014) Extraction and characterization of keratin from bovine hoof: a potential material for biomedical applications. SpringerPlus 3:596

Katoh K, Shibayama M, Tanabe T, Yamauchi K (2004) Preparation and physicochemical properties of compression-molded keratin films. Biomaterials 25:2265–2272. https://doi.org/10.1016/j.biomaterials.2003.09.021

Kim NK, Bhattacharyya D (2016) Development of fire resistant wool polymer composites: mechanical performance and fire simulation with design perspectives. Mater Des 106:391–403. https://doi.org/10.1016/j.matdes.2016.06.005

Kim NK, Lin RJT, Bhattacharyya D (2014) Extruded short wool fibre composites: mechanical and fire retardant properties. Compos Part B Eng 67:472–480. https://doi.org/10.1016/j.compositesb.2014.08.002

Kim NK, Lin RJT, Bhattacharyya D (2015) Effects of wool fibres, ammonium polyphosphate and polymer viscosity on the flammability and mechanical performance of PP/wool composites. Polym Degrad Stab 119:167–177. https://doi.org/10.1016/j.polymdegradstab.2015.05.015

Lai SM, Huang CK, Shen HF (2005) Preparation and properties of biodegradable poly(butylene succinate)/starch blends. J Appl Polym Sci 97:257–264. https://doi.org/10.1002/app.21679

Li J, Li Y, Li L, Mak AFT, Ko F, Qin L (2009) Preparation and biodegradation of electrospun PLLA/keratin nonwoven fibrous membrane. Polym Degrad Stab 94:1800–1807. https://doi.org/10.1016/j.polymdegradstab.2009.06.004

Liebeck B, Hidalgo N, Roth G, Popescu C, Böker A (2017) Synthesis and characterization of methyl cellulose/keratin hydrolysate composite membranes. Polymers 9:91

Lin H, Yan H, Liu B, Wei L, Xu B (2011) The influence of KH-550 on properties of ammonium polyphosphate and polypropylene flame retardant composites. Polym Degrad Stab 96:1382–1388. https://doi.org/10.1016/j.polymdegradstab.2011.03.016

Liu X, Xu W, Peng X (2009) Effects of stearic acid on the interface and performance of polypropylene/superfine down powder composites. Polym Compos 30:1854–1863. https://doi.org/10.1002/pc.20759

Liu X, Chen F, Yang H, Xu W (2013) Feasibility and properties of polypropylene composites reinforced with down feather whisker. J Thermoplast Compos Mater 28:19–31. https://doi.org/10.1177/0892705712475014

Martínez-Hernández AL, Velasco-Santos C, de-Icaza M, Castaño VM (2007) Dynamical–mechanical and thermal analysis of polymeric composites reinforced with keratin biofibers from chicken feathers. Compos Part B Eng 38:405–410. https://doi.org/10.1016/j.compositesb.2006.06.013

Metın D, Tihminlioğlu F, Balköse D, Ülkü S (2004) The effect of interfacial interactions on the mechanical properties of polypropylene/natural zeolite composites. Compos Part A Appl Sci Manuf 35:23–32. https://doi.org/10.1016/j.compositesa.2003.09.021

Mohanty AK, Misra M, Drzal LT (2002) Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. J Polym Environ 10:19–26. https://doi.org/10.1023/A:1021013921916

Mohanty S, Nayak SK, Verma SK, Tripathy SS (2004) Effect of MAPP as a coupling agent on the performance of jute–PP composites. J Reinf Plast Compos 23:625–637. https://doi.org/10.1177/0731684404032868

Netravali AN, Chabba S (2003) Composites get greener. Mater Today 6:22–29. https://doi.org/10.1016/S1369-7021(03)00427-9

Pardo-Ibáñez P, Lopez-Rubio A, Martínez-Sanz M, Cabedo L, Lagaron JM (2014) Keratin–polyhydroxyalkanoate melt-compounded composites with improved barrier properties of interest in food packaging applications. J Appl Polym Sci. https://doi.org/10.1002/app.39947

Poole AJ, Church JS, Huson MG (2009) Environmentally sustainable fibers from regenerated protein. Biomacromol 10:1–8. https://doi.org/10.1021/bm8010648

Poole A, Lyons R, Church J (2011) Dissolving feather keratin using sodium sulfide for bio-polymer applications. J Polym Environ 19:995–1004. https://doi.org/10.1007/s10924-011-0365-6

Pourjavaheri F, Jones OAH, Czajka M, Martinez-Pardo I, Blanch EW, Shanks RA (2018) Design and characterization of sustainable bio-composites from waste chicken feather keratin and thermoplastic polyurethane. Polym Compos 39:E620–E632. https://doi.org/10.1002/pc.24794

Rajkumar G, Srinivasan J, Suvitha L (2013) Development of novel silk/wool hybrid fibre polypropylene composites. Iran Polym J 22:277–284. https://doi.org/10.1007/s13726-013-0128-4

Rana AK, Mandal A, Bandyopadhyay S (2003) Short jute fiber reinforced polypropylene composites: effect of compatibiliser, impact modifier and fiber loading. Compos Sci Technol 63:801–806. https://doi.org/10.1016/S0266-3538(02)00267-1

Reddy N, Yang Y (2010) Light-weight polypropylene composites reinforced with whole chicken feathers. J Appl Polym Sci 116:3668–3675. https://doi.org/10.1002/app.31931

Reddy N, Jiang J, Yang Y (2014) Biodegradable composites containing chicken feathers as matrix and jute fibers as reinforcement. J Polym Environ 22:310–317. https://doi.org/10.1007/s10924-014-0648-9

Russell SJ, Institute T (2007) Handbook of Nonwovens. CRC Press, Cambridge

Sallih N, Lescher P, Bhattacharyya D (2014) Factorial study of material and process parameters on the mechanical properties of extruded kenaf fibre/polypropylene composite sheets. Compos Part A Appl Sci Manuf 61:91–107. https://doi.org/10.1016/j.compositesa.2014.02.014

Shavandi A, Ali MA (2019) Graft polymerization onto wool fibre for improved functionality. Prog Org Coat 130:182–199. https://doi.org/10.1016/j.porgcoat.2019.01.054

Shavandi A, Bekhit AE-DA, Carne A, Bekhit A (2016) Evaluation of keratin extraction from wool by chemical methods for bio-polymer application. J Bioact Compat Pol 32:163–177. https://doi.org/10.1177/0883911516662069

Shavandi A, Carne A, Bekhit AA, Bekhit AE-DA (2017a) An improved method for solubilisation of wool keratin using peracetic acid. JECE 5:1977–1984. https://doi.org/10.1016/j.jece.2017.03.043

Shavandi A, Silva TH, Bekhit AA, Bekhit AE-DA (2017b) Keratin: dissolution, extraction and biomedical application. Biomater Sci 5:1699–1735. https://doi.org/10.1039/C7BM00411G

Song K, Xu H, Xie K, Yang Y (2017) Keratin-based biocomposites reinforced and cross-linked with dual-functional cellulose nanocrystals. Acs Sustain Chem Eng 5:5669–5678. https://doi.org/10.1021/acssuschemeng.7b00085

Spiridon I, Paduraru OM, Rudowski M, Kozlowski M, Darie RN (2012) Assessment of changes due to accelerated weathering of low-density polyethylene/feather composites. Ind Eng Chem Res 51:7279–7286. https://doi.org/10.1021/ie300738d

Supri AG, Aizat AE, Yazid MIM, Masturina M (2013) Chicken feather fibers–recycled high-density polyethylene composites: the effect of ε-caprolactam. J Thermoplast Compos Mater 28:327–339. https://doi.org/10.1177/0892705713484746

Torres FG, Cubillas ML (2005) Study of the interfacial properties of natural fibre reinforced polyethylene. Polym Test 24:694–698. https://doi.org/10.1016/j.polymertesting.2005.05.004

Wambua P, Ivens J, Verpoest I (2003) Natural fibres: can they replace glass in fibre reinforced plastics? Compos Sci Technol 63:1259–1264. https://doi.org/10.1016/S0266-3538(03)00096-4

Willett JL, Felker FC (2005) Tensile yield properties of starch-filled poly(ester amide) materials. Polymer 46:3035–3042. https://doi.org/10.1016/j.polymer.2005.01.059

Xie Y, Hill CAS, Xiao Z, Militz H, Mai C (2010) Silane coupling agents used for natural fiber/polymer composites: a review. Compos Part A Appl Sci Manuf 41:806–819. https://doi.org/10.1016/j.compositesa.2010.03.005

Xu W, Wang X, Li W, Peng X, Liu X, Wang XG (2007) Characterization of superfine wool powder/poly(propylene) blend film. Macromol Mater Eng 292:674–680. https://doi.org/10.1002/mame.200600491

Zhan M, Wool RP (2010) Biobased composite resins design for electronic materials. J Appl Polym Sci 118:3274–3283. https://doi.org/10.1002/app.32633

Zhan M, Wool RP, Xiao JQ (2011) Electrical properties of chicken feather fiber reinforced epoxy composites. Compos Part A Appl Sci Manuf 42:229–233. https://doi.org/10.1016/j.compositesa.2010.11.007

Zhang Q, Liebeck BM, Yan K, Demco DE, Körner A, Popescu C (2012) Alpha-helix self-assembly of oligopeptides originated from beta-sheet keratin. Macromol Chem Phys 213:2628–2638. https://doi.org/10.1002/macp.201200446